

OPTIMIZATION OF THE PERFORMANCE OF A POLYURETHANE ADHESIVE SYSTEM
OVER THE TEMPERATURE RANGE OF -423°F TO +200°F

By

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FOREWORD

This report was prepared by Whittaker Corporation, Narmco Research & Development Division, under Contract NAS 8-11958, entitled "Optimization of the Performance of a Polyurethane Adhesive System over the Temperature Range of -423°F to $+200^{\circ}\text{F}$," for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Materials Division, of the George C. Marshall Space Flight Center with Mr. L. M. Thompson acting as Project Manager. The research was conducted in Narmco's Laboratory by Messrs. A. McLeod, D. Steele, and R. Empey. Mr. H. Holland served as program manager. This report covers the period from 14 May 1966 to 14 February 1967.

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ABSTRACT

The bond performance of Narmco 7343 adhesive was evaluated during long-term storage (8 months) at high humidity and during short-term storage (28 days) at ambient conditions. Strength retention was greatest when siloxane primers were used in combination with siloxane integral blends.

When similar polyurethane adhesives were blended with Narmco 7343 adhesive, the room temperature and +200°F strengths improved significantly, with no sacrifice of -320°F strength. A direct correlation among Shore D hardness, NCO content, and strength was established.

Slower reacting amine curing agents were studied in an attempt to increase the pot life of the higher strength adhesives obtained when Narmco 7343 was blended with similar polyurethane adhesives. Narmco 7148 curing agent increased pot life about fivefold; when it was used in the form of a super-cooled liquid, pot life was increased about tenfold.

Several bonding process changes were examined to establish their effect on bond strength. Small improvements were noted when a hand emulsifier was used to mix in the curing agent and when the degassing step was eliminated.

Approximately 13,500 Bell peel and lap shear bonded specimens were tested at -320°F, room temperature, and +200°F as the primary means for evaluating individual studies.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY	2
DISCUSSION	4
Effect of Various Priming Procedures on Narmco 7343 Adhesive Bond Strength	4
Application Method of Z-6040 Siloxane Primer	4
Effect of Hydrolyzed Z-6040 Primer on Room Temperature Bond Strength.	4
Effect of Hydrolyzed Z-6020 Primer on Room Temperature Bond Strength	12
Effect of Epoxy Primer on Room Temperature Bond Strength	12
Effect of Integrally Blending Siloxane Coupling Agents with Narmco 7343 Adhesive	16
Combined Effect of Z-6040 Siloxane/7343 Integral Blend with Hydrolyzed Z-6040 Siloxane Primer	20
Shelf Life of Z-6040/7343 Blend	20
Effect of Humidity on Narmco 7343 Adhesive	20
Extended Time Humid Storage Study.	23
Specimen Dry Storage versus Ambient Storage	23
Reversible Effect of Water Adsorption	40
Effect of Various Formulations on Narmco 7343/7139 Adhesive System	46
Effect of Various Curing Agent Concentrations on Bond Strength	46
Effect of Water Concentrations on Room Temperature Bond Strength	46

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Effect of Polyol Co-Curing Agent on Room Temperature Bond Strength	50
Aluminum and Aluminum Oxide Fillers	54
Toluene Diisocyanate Concentrations	54
Effect of Processing Changes on Narmco 7343/7139 Adhesive System	57
Effect of Various Mixing Procedures on Room Temperature Bond Strengths	57
Effect of a Nondegassed Adhesive Procedure on Bond Strength	58
Effect of a Scrim Cloth Carrier on Room Temperature Bond Strength	58
Effect of an Adherend Alkaline Cleaner on Room Temperature Bond Strength	64
Room Temperature Strengths on Bonds Prepared in Accordance with a Procedure Suggested by the Contracting Agency	64
Effect of Various 140°F Postcure Cycles on Room Temperature Bond Strength	68
Effect of Time between Mixing and Layup on Room Temperature Bond Strength	68
Effect of Blends of Polyurethane Adhesives	68
Slow Amine Curing Agents	74
EXPERIMENTAL	85
CONCLUSIONS	103
RECOMMENDED FUTURE WORK	104
REFERENCES	105

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY	2
DISCUSSION	4
Effect of Various Priming Procedures on Narmco 7343 Adhesive Bond Strength	4
Application Method of Z-6040 Siloxane Primer	4
Effect of Hydrolyzed Z-6040 Primer on Room Temperature Bond Strength.	4
Effect of Hydrolyzed Z-6020 Primer on Room Temperature Bond Strength	12
Effect of Epoxy Primer on Room Temperature Bond Strength	12
Effect of Integrally Blending Siloxane Coupling Agents with Narmco 7343 Adhesive	16
Combined Effect of Z-6040 Siloxane/7343 Integral Blend with Hydrolyzed Z-6040 Siloxane Primer	20
Shelf Life of Z-6040/7343 Blend	20
Effect of Humidity on Narmco 7343 Adhesive	20
Extended Time Humid Storage Study.	23
Specimen Dry Storage versus Ambient Storage	23
Reversible Effect of Water Adsorption	40
Effect of Various Formulations on Narmco 7343/7139 Adhesive System	46
Effect of Various Curing Agent Concentrations on Bond Strength	46
Effect of Water Concentrations on Room Temperature Bond Strength	46

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Effect of Polyol Co-Curing Agent on Room Temperature Bond Strength	50
Aluminum and Aluminum Oxide Fillers	54
Toluene Diisocyanate Concentrations	54
Effect of Processing Changes on Narmco 7343/7139 Adhesive System	57
Effect of Various Mixing Procedures on Room Temperature Bond Strengths	57
Effect of a Nondegassed Adhesive Procedure on Bond Strength	58
Effect of a Scrim Cloth Carrier on Room Temperature Bond Strength	58
Effect of an Adherend Alkaline Cleaner on Room Temperature Bond Strength	64
Room Temperature Strengths on Bonds Prepared in Accordance with a Procedure Suggested by the Contracting Agency	64
Effect of Various 140°F Postcure Cycles on Room Temperature Bond Strength	68
Effect of Time between Mixing and Layup on Room Temperature Bond Strength	68
Effect of Blends of Polyurethane Adhesives	68
Slow Amine Curing Agents	74
EXPERIMENTAL	85
CONCLUSIONS	103
RECOMMENDED FUTURE WORK	104
REFERENCES	105

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY	2
DISCUSSION	4
Effect of Various Priming Procedures on Narmco 7343 Adhesive Bond Strength	4
Application Method of Z-6040 Siloxane Primer	4
Effect of Hydrolyzed Z-6040 Primer on Room Temperature Bond Strength.	4
Effect of Hydrolyzed Z-6020 Primer on Room Temperature Bond Strength	12
Effect of Epoxy Primer on Room Temperature Bond Strength	12
Effect of Integrally Blending Siloxane Coupling Agents with Narmco 7343 Adhesive	16
Combined Effect of Z-6040 Siloxane/7343 Integral Blend with Hydrolyzed Z-6040 Siloxane Primer	20
Shelf Life of Z-6040/7343 Blend	20
Effect of Humidity on Narmco 7343 Adhesive	20
Extended Time Humid Storage Study.	23
Specimen Dry Storage versus Ambient Storage	23
Reversible Effect of Water Adsorption	40
Effect of Various Formulations on Narmco 7343/7139 Adhesive System	46
Effect of Various Curing Agent Concentrations on Bond Strength	46
Effect of Water Concentrations on Room Temperature Bond Strength	46

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Effect of Polyol Co-Curing Agent on Room Temperature Bond Strength	50
Aluminum and Aluminum Oxide Fillers	54
Toluene Diisocyanate Concentrations	54
Effect of Processing Changes on Narmco 7343/7139 Adhesive System	57
Effect of Various Mixing Procedures on Room Temperature Bond Strengths	57
Effect of a Nondegassed Adhesive Floccules on Bond Strength	58
Effect of a Scrim Cloth Carrier on Room Temperature Bond Strength	58
Effect of an Adherent Alkaline Cleaner on Room Temperature Bond Strength	64
Room Temperature Strengths on Bonds Prepared in Accordance with a Procedure Suggested by the Contracting Agency	64
Effect of Various 140°F Postcure Cycles on Room Temperature Bond Strength	68
Effect of Time between Mixing and Layup on Room Temperature Bond Strength	68
Effect of Blends of Polyurethane Adhesives	68
Slow Amine Curing Agents	74
EXPERIMENTAL	85
CONCLUSIONS	103
RECOMMENDED FUTURE WORK	104
REFERENCES	105

TABLE OF CONTENTS (Continued)

	<u>Page</u>
APPENDIX A. Average Strength of Bonds Made by Various Procedures	107
APPENDIX B. Recommended Bond Procedure for Narmco 7343 Cryogenic Adhesive	111
APPENDIX C. Quality Control Data	117
APPENDIX D. Determination of Shear Strength of Adhesive Bonded Metal-to-Metal Specimens at Room Temperature and Elevated Temperatures	123
APPENDIX E. Determination of Bell Peel Strength of Adhesive Bonded Metal-to-Metal Specimens at Room Temperature, Cryogenic and Elevated Temperatures	135
APPENDIX F. Source of Materials List	143

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Effect of Storage Time of Uncatalyzed 1.0-phr Z-6040/7343 Integral Blend on Room Temperature Bond Strength	22
2	Effect of Humid Storage Time on Primed and Nonprimed -320°F Bell Peel Strength	24
3	Effect of Humid Storage Time on Primed and Nonprimed Room Temperature Bell Peel Strength	25
4	Effect of Humid Storage Time on Primed and Nonprimed +200°F Bell Peel Strength	26
5	Effect of Humid Storage Time on Primed and Nonprimed -320°F Lap Shear Strength	27
6	Effect of Humid Storage Time on Primed and Nonprimed Room Temperature Lap Shear Strength	28
7	Effect of Humid Storage Time on Primed and Nonprimed +200°F Lap Shear Strength	29
8	Effect of Ambient and Dry Storage Time on Nonprimed Room Temperature Bond Strengths	33
9	Effect of Ambient and Dry Storage Time on Nonprimed and Z-6040 Hydrolyzed Primed Plus Z-6040 Integral Blend Room Temperature Lap Shear Strengths	41
10	Effect of Ambient and Dry Storage Time on Nonprimed and Z-6040 Hydrolyzed Primed Plus Z-6040 Integral Blend Room Temperature Bell Peel Strengths	42
11	Effect of Apco 1510 Urethane Coating on Z-6040 Hydrolyzed Primed Plus Z-6040 Integral Blend Room Temperature Lap Shear and Bell Peel Strengths	44
12	Effect of 7139 Curing Agent Concentration on Lap Shear Strength	49
13	Mechanical Mixers	60
14	Effect of Void Content on Room Temperature Lap Shear Strength	61

LIST OF FIGURES (Continued)

<u>Figure</u>		<u>Page</u>
15	Effect of Narmco 7343 on Bond Strength	73
16	Comparison of Shore D Hardness and Lap Shear Strength for Various Polyurethane Adhesive Blends.	75
17	Effect of Prepolymer NCO Content on Room Temperature Lap Shear Strength for Various Polyurethane Adhesive Blends	76
18	Comparison of Room Temperature Lap Shear Strength and Usable Pot Life for Various Polyurethane Adhesive Blends	77
19	Pot Life of 7343/7348 Blends with 7139 and Dry 7148 Curing Agents	80
20	Deburring of Bell Peel and Lap Shear Panel Adherends.	90
21	Removal of Mill Lettering with Methyl Ethyl Ketone (MEK)	90
22	Vapor Degreasing of Bell Peel Panel Adherends with Trichloroethylene	91
23	Etching of Bell Peel Panel Adherends with Sulfuric Acid/Sodium Dichromate/Water Solution	91
24	Distilled Water Rinse after Etching.	92
25	Oven Drying of Bell Peel Panel Adherends at 140°-150°F	92
26	Tape Masking of Nonfaying Surface of Bell Peel Panel Adherend	93
27	Tape Masking at Faying Side in the Peel Initiation Area	93
28	Spray Application of Siloxane Primer to Bell Peel Panel Adherend	94
29	Placing of Narmco 7343 Prepolymer and Narmco 7139 Curing Agent in Vacuum Oven	94

LIST OF FIGURES (Continued)

<u>Figure</u>		<u>Page</u>
30	Heating and Degassing of Narmco 7343 Prepolymer and Narmco 7139 Curing Agent in Vacuum Oven	95
31	Mixing of Adhesive and Curing Agent in a Hobart Eccentric Rotary Mixer.	95
32	Bell Peel and Lap Shear Panel Adherends Preparatory to Daily Layup Operation	96
33	Application and Spreading of Adhesive to Faying Surfaces of Bell Peel Panel Adherends	96
34	Application and Spreading of Adhesive to Faying Surfaces of Lap Shear Panel Doublers.	97
35	Application of Adhesive to Faying Overlap Area of Lap Shear Panel Adherend	97
36	Applying Glass Beads to Spread Adhesive for Bondline Thickness Control	98
37	Uniting the Bell Peel Panel Components After the Adhesive Has Been Applied	98
38	Stacking Assembled Bell Peel Panels on the Curing Fixture	99
39	Interposing Fluorocarbon Fabric as Separator Films Between Panels	99
40	Stacking Lap Shear Panels and Doubler Panels on the Curing Fixture	100
41	Stacked Bell Peel Panels on Curing Fixture Being Pressed at Room Temperature and 25 psi to Close Adherends to Glass Beads.	100
42	Inserting Curing Fixture with Assembled Panels into Envelope Vacuum Bag	101
43	Bell Peel and Lap Shear Panels Undergoing Overnight (16-19 hours) Room Temperature Cure at 10-15 in. Hg Vacuum Pressure	101
44	Lap Shear Test Specimen	102
45	Bell Peel Panel with Three Bell Peel Test Coupons	102

LIST OF FIGURES (Continued)

<u>Figure</u>		<u>Page</u>
46	Test Specimen	125
47	Preferred Assembled Panel	126
48	Test Fixture	127
49	Prototype, or Dummy Specimen.	128
50	Test Apparatus Assembly	129
51	Test Panel and Finished Test Specimen	137
52	Peel Test Fixture	138
53	Test Fixture with Specimen Installed for Room Temperature Test	140

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Effect of Z-6040 Primer Concentration on Room Temperature Bond Strength	5
2	Effect of Time Between Z-6040 Priming and Bonding on Room Temperature Bond Strength	5
3	Effect of Solvent Rinse 1 Minute After Z-6040 Spray Prime on Room Temperature Bond Strength	6
4	Effect of Z-6040 Dip Time on Room Temperature Bond Strength	6
5	Test Data for Bonds Made with Hydrolyzed Z-6040 Siloxane Primer	8
6	Effect of Time Between Mixing and Applying Z-6040 Hydrolyzed Siloxane Primer	8
7	Effect of Hydrolyzed Z-6040 Primer on Room Temperature Bond Strength	9
8	Effect of Hydrolyzed Z-6040 Siloxane Primer Spray Pass Speed on Room Temperature Lap Shear Strength	10
9	Effect of Z-6040 Hydrolyzed Siloxane Primer Concentration on Room Temperature Bond Strength	10
10	Effect of Z-6040 Hydrolyzed Primer Concentration on Room Temperature Bond Strength	11
11	Effect of Hydrolyzed Z-6040 Primer Concentration on Humid Storage Bond Strength Retention	11
12	Effect of Residual Acetic Acid on Room Temperature Lap Shear Strength	13
13	Effect of a Hydrolyzed Z-6040 Siloxane Primer Cure Cycle on Room Temperature Lap Shear Strength	13
14	Comparison of Z-6020 and Z-6040 Hydrolyzed Siloxane Primers on Room Temperature Bond Strengths	14
15	Strength of Bonds with Adhesive Applied at Various Times After Priming with Epon 828/Versamid 125	15
16	Effect of Epoxy Primers on Room Temperature Bond Strength	17

LIST OF TABLES (Continued)

<u>Table</u>		<u>Page</u>
17	Adherend Primers used with Narmco 7343 Adhesive	18
18	Room Temperature Strengths of Siloxane Primed and Siloxane Integral Blend Bonds	19
19	Effect of Z-6040 Siloxane/7343 Integral Blend with Hydrolyzed Z-6040 Siloxane Primer	21
20	Comparison of Room Temperature Bond Strength for Bonds Made by Bonding Procedures 8 and 10	30
21	Comparison of -320°F Bond Strength for Bonds Made by Bonding Procedures 8 and 10	31
22	Comparison of +200°F Bond Strength for Bonds Made by Bonding Procedures 8 and 10	31
23	Effect of Ambient and Dry Storage Time on Room Temperature Nonprimed Bond Strengths	32
24	Comparison of Room Temperature Z-6020 Siloxane Primed Bond Strength Stored under Dry and Ambient Conditions	34
25	Comparison of -320°F Z-6040 Siloxane Integral Blend Bond Strength Stored under Dry and Ambient Conditions	34
26	Comparison of Room Temperature Z-6040/7343 Siloxane Integral Blend Bond Strength Stored under Dry and Ambient Conditions	35
27	Comparison of +200°F Z-6040 Siloxane Integral Blend Bond Strength Stored under Dry and Ambient Conditions	35
28	Comparison of -320°F Z-6040 Hydrolyzed Siloxane Primed Bond Strength Stored under Dry and Ambient Conditions	36
29	Comparison of Room Temperature Z-6040 Hydrolyzed Siloxane Primed Bond Strength Stored under Dry and Ambient Conditions	36
30	Comparison of +200°F Z-6040 Hydrolyzed Siloxane Primed Bond Strength Stored under Dry and Ambient Conditions	37

LIST OF TABLES (Continued)

<u>Table</u>		<u>Page</u>
31	Comparison of Bonding Procedures with % Change from Dry Storage Conditions at Room Temperature, +200°F, and -320°F	38
32	Effect of Ambient and Dry Storage on Room Temperature Z-6040 Hydrolyzed Primed Plus Z-6040 Integral Blended Bond Strengths	39
33	Effect of Ambient Storage on Room Temperature Bond Strength of Z-6040 Hydrolyzed Plus Z-6040 Integral Blended Bonds Coated with Apco 1510 Coating for Urethane Adhesives	43
34	Effect of Drying Bonds Stored at 100% Relative Humidity	45
35	Effect of Narmco 7139 Curing Agent Concentration on Bell Peel Strength	47
36	Effect of Narmco 7139 Curing Agent Concentration on Lap Shear Strength	48
37	Effect of Open Time of Spread Adhesive on Room Temperature Bond Strength	51
38	Effect of Water Concentration on Bond Strength for Bonds Made Using Constant Total Stoichiometry	52
39	Effect of Water Concentration on Bond Strength for Bonds Made Using Constant Amine Curing Agent Concentration	53
40	Effect of Polyol Co-Curing Agent on Room Temperature Bond Strength	55
41	Effect of Fillers on Room Temperature Bond Strength	56
42	Effect of Toluene Diisocyanate Concentration on Room Temperature Bond Strength	57
43	Effect of Various Mixing Procedures on Room Temperature Bond Strength	59
44	Comparison of Degassed and Nondegassed Procedures on Room Temperature Bond Strength	62

LIST OF TABLES (Continued)

<u>Table</u>		<u>Page</u>
45	Comparison of Degassed and Nondegassed Procedures on -320°F Bond Strength	63
46	Effect of 112-112 Scrim Cloth on Nonprimed Room Temperature Bond Strength	64
47	Effect of an Adherend Alkaline Cleaner on Room Temperature Bond Strength	65
48	Comparison of Difference Between the Contracting Agency's Suggested Cure Cycle and Bonding Pro- cedure 10	66
49	Room Temperature Strength of Bonds Prepared in Accordance with a Procedure Suggested by the Contracting Agency	67
50	Effect of Various 140°F Postcure Cycles on Room Temperature Bond Strength	69
51	Effect of Time Between Mixing and Layup of Narmco 7343 Adhesive on Bond Strength	70
52	Effect of Narmco 7348 Concentration on Bond Strength	71
53	Effect of Various Polyurethane Prepolymer Blends on Bond Strength	72
54	Effect of Z-6040 Primer and Z-6040 Integral Blend	78
55	Effect of 2-Hour Water Boil on Narmco 7343 and 7348 Adhesive	78
56	Comparison Between Narmco 7139 and 7348 Curing Agents with Narmco 7348 Adhesive	81
57	Blends of Narmco 7343 and 7348 Cured with Narmco 7148 Adhesive	82
58	Comparison of Curing Agents	84
59	Bond Procedures	88
60	Average Strengths of Bonds Made by Various Procedures	108

LIST OF TABLES (Continued)

<u>Table</u>	<u>Page</u>
61 Quality Control Data for Narmco 7343 Prepolymer	119
62 Quality Control Data for Narmco Prepolymers	122
63 Quality Control Data for Narmco 7139 Curing Agent	122
64 Quality Control Data for Narmco 7148 Curing Agent	122

INTRODUCTION

During a recent NASA-sponsored program (Contract NAS 8-1565), several polymer systems were studied and evaluated as adhesives for applications at cryogenic temperatures. Resulting information from that program and other supporting information led to the general acceptance of the polyether-based polyurethane polymer as the most promising material for a cryogenic adhesive. The polyether-based isocyanate prepolymer (Narmco 7343) and the associated curing agent (Narmco 7139), originated during the performance of the above-mentioned program, produced adhesive bonds at cryogenic temperatures which were superior to those of other polymers. Subsequent use of the adhesive for structural applications, however, resulted in wide variations in bond performance, particularly with respect to peel strength. The source of this performance variation eluded early attempts at identification, and gave rise to the need for a concerted research effort to obtain performance consistency. Accordingly, the purpose of this research effort was to determine those factors which contribute to the variation in adhesive performance of Narmco 7343 resin over the temperature range from -423°F to $+200^{\circ}\text{F}$, and to incorporate these findings into bonding techniques specifically developed to eliminate or minimize variations in bond characteristics.

Program work carried out during the prior year involved a number of studies within the categories of materials characterization, bonding processes, bondline configuration, and strength retention of stored bonds. The work uncovered several factors thought to be responsible for variations in bond strength performance of Narmco 7343 adhesive. Variation in bondline thickness was determined to be an important factor affecting peel strength at room temperature and $+150^{\circ}\text{F}$. Variation in bond strength also occurred when testing was conducted before the optimum cure had been reached. High humidity was found to be the major factor responsible for the gradual degradation of bond strengths. It was determined that siloxane primers such as Dow Corning Z-6020 or Z-6040 not only greatly improved strength, but also provided a means of reducing the adverse effect of humidity.

Approximately 12,500 Bell peel and lap shear bonded specimens were prepared and tested at -320°F , room temperature, and $+150^{\circ}\text{F}$ as the primary means for evaluating individual studies.

The work reported herein describes a number of studies which were carried out in the continuing effort to improve the performance of Narmco 7343 adhesive. As was the case during the prior year, the primary means for study evaluation consisted of preparing and testing Bell peel and lap shear bonded specimens. Approximately 13,500 bonds were evaluated during the period herein reported.

SUMMARY

The observed improvement in bond strength and humid strength retention afforded by the use of siloxane primers led to further studies involving application methods, siloxane concentrations, siloxane hydrolyzation, and the blending of siloxane with Narmco 7343 adhesive. Several epoxy primers were also evaluated. Test data from these studies indicate that siloxane primers or blends generally improve bond strength when compared to nonprimed specimens. Improvement was greatest when hydrolyzed Z-6040 siloxane primer was used in combination with Z-6040 integrally blended with Narmco 7343 adhesive.

The observed strength losses at 100% RH prompted further studies of long-term storage effects (8 months). The bond strength retention of both the siloxane primed and nonprimed specimens leveled off after a serious initial loss; after this time, however, the siloxane primed bonds remained superior. The effect of short-term ambient storage (50%-60% RH) on nonprimed and siloxane-treated bond strength was also studied. Test data showed that nonprimed bonds gradually lost strength; however, bonds incorporating the hydrolyzed Z-6040 siloxane primer and the Z-6040 integral blend displayed excellent strength retention. It was shown in related work that about 70% of the initial nonprimed bond strength can be regained when specimens are dried after being stored in a humid environment. Recovery is apparently due to the reversal of water plasticization.

Several variations in adhesive formulation were studied in an attempt to improve bond performance. The effect of various curing agent concentrations, adsorption of water during layup, addition of water to the adhesive, use of polyol co-curing agent, addition of aluminum and aluminum oxide fillers, and addition of toluene diisocyanate were evaluated. No significant improvement in overall bond strength performance was achieved by these formulation changes.

The effects of several bonding process changes were examined, including mixing of the curing agent, elimination of the degassing step, addition of a scrim cloth carrier, addition of an adherend alkaline cleaning step, use of various 140°F postcure cycles, and varying the times between mixing and bond layup. It was concluded that some improvement in bond strength was obtained when curing agent was mixed with a hand-operated emulsifier. A small improvement in -320°F bond strength was obtained when the degassing step was eliminated. The remaining processing changes produced little or no strength improvement.

Several polyurethane adhesives with various NCO contents were blended with Narmco 7343. A direct correlation among Shore D hardness, NCO content, and bond strength was established. Significant and steady improvement in room temperature and elevated temperature strengths was obtained as NCO content was increased.

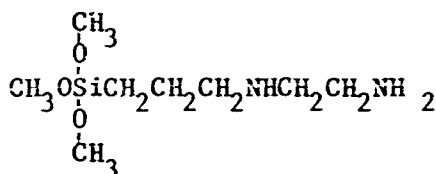
While the harder and presumably less elastic adhesive, yielded greatly improved bond strengths, the usable processing pot life was drastically reduced. Slower reacting, hindered amine curing agents were therefore investigated; with the several studied, Narmco 7148 increased pot life fivefold and bond strength retention was excellent. Narmco 7148 as a super-cooled liquid increased pot life tenfold; however, no strength data were obtained.

DISCUSSION

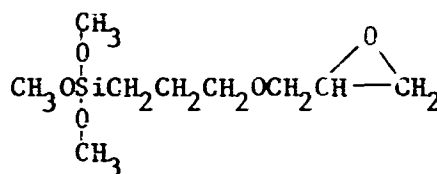
Effect of Various Priming Procedures on Narmco 7343 Adhesive Bond Strength

Work during the previous period showed that siloxane primers lessened the effect of humidity on the bond strength and at the same time greatly improved the bond strength. However, the adverse effects of humidity were not entirely overcome by these primers and they apparently caused a wider spread in the data.

Dow Corning Z-6020 primer gave very high initial bond strengths, but the primer was much more affected by humidity than was Dow Corning Z-6040 primer. At the end of 8 weeks at 100% RH, the Z-6040 primed bonds tested stronger than the Z-6020 primed bonds. Studies of various priming procedures carried out during the current period are discussed below.



Z-6020



Z-6040

Application Method of Z-6040 Siloxane Primer. - The data spread resulting from the use of siloxane primers may have been caused by nonuniform application of the primer and/or nonoptimum primer concentrations. Several studies were therefore conducted in an attempt to improve primer application techniques.

The results of these studies are shown in Tables 1 through 4. There was almost no trend with primer concentration over the range from 0.1 pph to 0.4 pph of Z-6040 siloxane, as shown in Table 1. The data in Table 2 indicate a possible slight improvement when panels primed with Z-6040 were allowed to cure at ambient conditions for 1 day prior to application of adhesive. Table 2 also reflects a change in solvent from anhydrous denatured ethyl alcohol* to anhydrous methanol, under the theory that the denaturants in the ethyl alcohol may be detrimental; however, the data do not support this theory. Rinsing the panels after the primer solvent evaporated did not affect the primer, as indicated by Table 3. However, data in Table 4 show that panels which were dipped for as long as 20 minutes in primer, then rinsed immediately after removal from the primer bath, displayed strengths about equal to bonds made with unprimed adherends.

Effect of Hydrolyzed Z-6040 Primer on Room Temperature Bond Strength. - As part of the continuing effort to develop an improved method of applying siloxane primers, Dow-Corning Z-6040 primer was hydrolyzed with dilute acetic acid prior to application.

* 100 volumes anhydrous ethanol, 1 volume methyl isobutyl ketone, 1 volume ethyl acetate, and 1 volume hydrocarbon solvent.

TABLE 1

EFFECT OF Z-6040 PRIMER CONCENTRATION ON ROOM TEMPERATURE BOND STRENGTH

Set No.	Primer * Concentration, pph	Lap Shear Strength, psi				Bell Peel Strength, piw			
		Avg	High	Low	N	Avg	High	Low	N
237	0.1	2437	3060	1750	24	91	102	83	9
237	0.2	2294	2840	1520	24	89	96	82	9
237	0.4	2092	2440	1540	24	95	100	91	9

* Z-6040 in anhydrous methanol.

N = number of specimens tested.

TABLE 2

EFFECT OF TIME BETWEEN Z-6040 PRIMING AND BONDING
ON ROOM TEMPERATURE BOND STRENGTH

Set No.	Time Between Priming & Bonding	Lap Shear Strength, psi				Bell Peel Strength, p/w			
		Avg	High	Low	N	Avg	High	Low	N
236*	2 hr	2634	3210	2100	24	102	109	95	9
237*	26 hr	2892	3320	2400	24	101	116	95	9
237**	2 hr	2294	2840	1520	24	89	96	82	9

* Concentration 0.2 pph Z-6040 in anhydrous denatured ethanol.

** Concentration 0.2 pph Z-6040 in anhydrous methanol.

TABLE 3

EFFECT OF SOLVENT RINSE 1 MINUTE AFTER Z-6040 SPRAY PRIME
ON ROOM TEMPERATURE BOND STRENGTH

Set No.	Ethanol Rinse	Lap Shear Strength, psi			Bell Peel Strength, pli		
		Avg	High	Low	Avg	High	Low
236	Yes	2634	3210	2100	102	109	95
236	No	2674	3360	2040	103	107	98

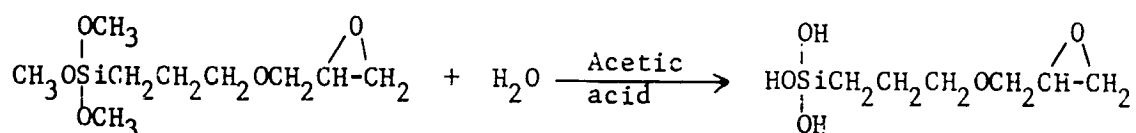
Note: Concentration 0.2 pph of Z-6040 in anhydrous denatured ethanol.

TABLE 4

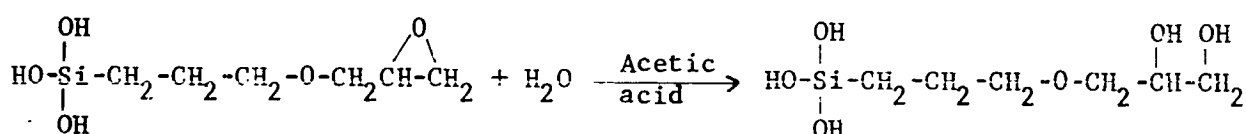
EFFECT OF Z-6040 DIP TIME ON ROOM TEMPERATURE BOND STRENGTH

Set No.	Dip Time, min	Lap Shear Strength, psi			Bell Peel Strength, pli		
		Avg	High	Low	Avg	High	Low
239	0.5	1230	2000	1290	51	57	47
239	3.0	1667	2300	1340	50	53	46
239	20.0	1669	2080	1430	53	55	48

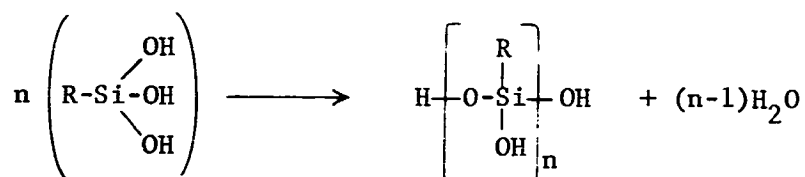
Note: Concentration 0.20 pph of Z-6040 in anhydrous methanol.



The acetic acid acts as a catalyst to convert the methoxy groups on the Z-6040 to silanol groups. At the same time, it is probable that it opens at least part of the epoxy rings to form a glycol. The glycol as well as the residual epoxy groups is capable of reacting with the 7343/7139 adhesive system to



form strong chemical bonds. The newly formed silanol groups are more reactive toward the aluminum than methoxy groups and, as a result, should produce better bonding to the aluminum. These silanol groups are also co-reactive, forming a polysiloxane; as a result, the primer is stable for only a few minutes before the solution begins to cloud.



The test results for a large number of bonds made with hydrolyzed Z-6040 siloxane primer and stored about 8 days at ambient conditions prior to test are listed in Table 5. While these strengths are not as high as those of dry-stored bonds made with Z-6020 siloxane primer (Procedure 9), they appear to be higher than those of other bonds stored at ambient conditions (see Appendix A). These findings were repeatedly confirmed by other studies, discussed elsewhere in this report.

Several studies were conducted which involved varying the time of application of the hydrolyzed Z-6040 primer. Table 6 is a comparison of the results obtained from a study in which a batch of primer was applied to the adherends at various times after mixing. The hydrolyzed primer polymerized on standing, and caused the primer solution to turn cloudy a few minutes after mixing. This study compared bonds made with primer that was initially clear (2 minutes) with varying degrees of reaction through an almost milky solution (1 hour). The results indicated that bond strengths were about equivalent; however, the higher molecular weight primer (1 hour) may not be quite as good as primer applied sooner.

The results of a number of studies on hydrolyzed Z-6040 siloxane primer concentration are shown in Tables 7 through 11. The data in the tables are conflicting, as Tables 7 through 9 appear to indicate that the optimum primer concentration is below 0.2 pph, while Tables 10 and 11 indicate the opposite. Because of this conflict, no change was made from the 0.2-pph concentration.

TABLE 5

TEST DATA FOR BONDS MADE WITH HYDROLYZED Z-6040 SILOXANE PRIMER

	Bell Peel Strength, piw			Lap Shear Strength, psi		
	-320°F	RT	+200°F	-320°F	RT	+200°F
Average	73	68	69	8426	3122	1725
High	89	134	94	9200	4750	3000
Low	56	34	40	5300	1460	625
No. Tested	18	81	18	64	448	64

TABLE 6

EFFECT OF TIME BETWEEN MIXING AND APPLYING
Z-6040 HYDROLYZED SILOXANE PRIMER

Time Between Mixing and Applying Primer, min	RT Lap Shear Strength, psi			
	Avg	High	Low	N
2	2935	3680	2100	32
15	3000	4080	2260	32
30	2990	3750	1230	32
60	2780	3450	1940	32

TABLE 7

EFFECT OF HYDROLYZED Z-6040 PRIMER ON ROOM TEMPERATURE BOND STRENGTH

Set No.	Primer Formulation	Concentration pph	RT Bell Peel Strength, piw				RT Lap Shear Strength, psi			
			Avg	High	Low	N	Avg	High	Low	N
251	0.2 g Z-6040 (Not hydrolyzed) 100 g methanol	0.2	43	54	29	9	2740	3780	1940	32
251	11 g Solution A* 90 g methanol	1.0	17	25	14	9	2500	3190	1800	32
251	2.2 g Solution A* 8 g water 90 g methanol	0.2	43	47	38	9	2900	3780	1850	16

* Solution A: 10 g Z-6040 in 100 g of 1.0% solution of acetic acid stirred 10 min until clear.

N = number of specimens tested.

TABLE 8

EFFECT OF HYDROLYZED Z-6040 SILOXANE PRIMER
 SPRAY PASS SPEED ON ROOM TEMPERATURE LAP SHEAR STRENGTH

Primer Spray Pass Speed	Avg, psi	High	Low	No. Tested
Fast	3150	4100	2060	32
↓	3020	4060	1700	32
Very Slow	3000	3920	2060	32
	2680	4100	1640	32

TABLE 9

EFFECT OF Z-6040 HYDROLYZED SILOXANE PRIMER CONCENTRATION
 ON ROOM TEMPERATURE LAP SHEAR STRENGTH

Set No.	Primer Concentration, pph	Avg, psi	High, psi	Low, psi	No. Tested
288	0.05	3900	4440	3370	16
288	0.20	3310	4680	2290	32

TABLE 10

EFFECT OF Z-6040 HYDROLYZED PRIMER CONCENTRATION ON ROOM TEMPERATURE BOND STRENGTH

Set No.	Z-6040 Hydrolyzed Primer Concentration, pph	Lap Shear Strength, psi				Bell Peel Strength, piw			
		Avg	High	Low	N	Avg	High	Low	N
308	0.01	2670	3380	1700	32	84	98	75	9
308	0.03	2930	3600	2100	32	117	124	110	9
308	0.10	3100	4200	2000	32	109	114	105	9
308	0.30	3470	4600	1650	32	127	138	118	9
308	1.00	3290	4450	2150	32	136	140	130	9

N = number of specimens tested.

TABLE 11

EFFECT OF HYDROLYZED Z-6040 PRIMER CONCENTRATION ON HUMID STORAGE BOND STRENGTH RETENTION

Set No.	Primer Concentration, pph	Storage Condition	Lap Shear Strength, psi				Bell Peel Strength, piw			
			Avg	High	Low	N	Avg	High	Low	N
300	0.2	Initial	2780	3470	1980	32	117	134	111	9
		4 week @ 100% RH	2079	2480	1450	32	98	124	82	9
300	2.0	Initial	3190	4440	1480	32	109	125	101	9
		4 week @ 100% RH	2678	3160	1760	32	85	90	77	9

N = number of specimens tested.

Strength data from a study on the effect of residual acetic acid on bond strength are shown in Table 12. The acetic acid was used as a catalyst for hydrolyzing the Z-6040 primer and was carried along with the primer when it was applied to the aluminum adherends. While the acetic acid had about 2 hours to evaporate prior to bonding, it is probable that some acid might have still been present at the time of bonding. For this study, bonds were made with adherends primed in the normal manner with hydrolyzed Z-6040 siloxane, except that after the primer had dried, some of the adherends were washed free of acetic acid with water, while others were washed with a 1% acetic acid solution to leave a higher-than-normal amount of acid on the adherend. The results appeared to indicate that acetic acid is detrimental to bond performance, and that removal of excess acetic acid with a water rinse is beneficial.

A final study indicated that an elevated temperature cure of the hydrolyzed primer is detrimental, as shown in Table 13.

Effect of Hydrolyzed Z-6020 Primer on Room Temperature Bond Strength. -

Because of the indicated improvement resulting from hydrolyzation of Z-6040 siloxane primer before application, Z-6020 hydrolyzed siloxane primer was also investigated. Table 14 is a comparison of the results obtained from bonds made with Z-6040 and Z-6020 hydrolyzed primer (see Experimental Section). The data show that bond strengths are about equal. However, since the Z-6020 primer is not as good as Z-6040 primer in humid storage strength retention no further work was done with this primer.

Effect of Epoxy Primers on Room Temperature Bond Strength. - Epoxy adhesives are known for their excellent bond strength and good adhesion; however, the epoxies have generally displayed brittleness at cryogenic temperatures, and this results in low peel strengths. Several of these epoxy adhesives were studied as primers in very thin layers, in the hope that the thin layer would overcome the brittle nature of the epoxy while not affecting its adhesion.

One set of bonds, made in accordance with Bonding Procedure 10, included an adherend primer formulated from Epon 828 and Versamid 125 dissolved in toluene at 1% concentration by weight. The primer solution was applied by a spray method. Because this epoxy primer can react chemically with the adhesive, the adhesive application and bond layups were made at 1-, 3-, 7-, and 24-hour intervals in an attempt to determine an optimum application time. The results of the studies, shown in Table 15, show no trend in bond strengths with respect to time after priming, and strengths were no greater than those of prior bonds made with Z-6020. An attempt was made to follow the cure of the primer by infrared spectroscopy, but findings were inconclusive.

Another primer study was carried out using two other epoxy resins as primers. These flexible epoxy resins, Narmco X292 and X305, were selected on evidence of their bonding properties at cryogenic temperatures, which are superior to normal epoxies. Shell Z was used as the primer curing agent in

TABLE 12

EFFECT OF RESIDUAL ACETIC ACID ON ROOM TEMPERATURE LAP SHEAR STRENGTH

Wash	Avg, psi	High	Low	No. Tested
Water	3050	4100	1340	32
None	2870	3840	2220	32
1 % acetic acid	2350	3400	1600	32

TABLE 13

EFFECT OF A HYDROLYZED Z-6040 SILOXANE PRIMER CURE CYCLE
ON ROOM TEMPERATURE LAP SHEAR STRENGTH

Primer Cure Cycle	Avg, psi	High	Low	No. Tested
2 hr @ RT	2870	3840	2220	32
1 hr @ RT + 1 hr @ 160°F	2350	2870	1570	32

TABLE 14
COMPARISON OF Z-6020 & Z-6040 HYDROLYZED SILOXANE PRIMERS ON ROOM TEMPERATURE BOND STRENGTHS

Set No.	Hydrolyzed Primer	Concentration, pph	Lap Shear Strength, psi				Bell Peel Strength, piw			
			Avg	High	Low	N	Avg	High	Low	N
288	Z-6020	0.2	3230	4100	2080	32	65	81	55	9
288	Z-6040	0.2	3310	4680	2290	32	--	--	--	-

N = number of specimens tested.

TABLE 15

STRENGTH OF BONDS WITH ADHESIVE APPLIED AT VARIOUS TIMES
AFTER PRIMING WITH EPON 828/VERSAMID 125

Time after Prime, hr	Set No.	RT Bell Peel Strength, psi			RT Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low
1	207	43	49	35	9	2230	2787	1530
3	208	49	57	32	9	1870	2760	860
7	209	55	61	50	9	1908	2680	1200
24	210	50	55	46	9	2024	2640	1128

N = number of specimens tested.

both cases, and the primers were applied to the adherend by being wiped on the surface with a linen gauze saturated with the primer. The adherends were warmed to 150°F in order to achieve the desired thin primer layer. Adhesive application and bond layup were made after a 20-hour room temperature primer cure.

A final epoxy primer, formulated from 1% by weight Epon 828/Versamid 125 and 0.2% by weight Dow-Corning Z-6040 siloxane in toluene, was used to study the effect of an integrated epoxy/siloxane primer system. This primer was applied by the spray method. Adhesive application and bond layup were made after a 20-hour room temperature primer cure.

Room Temperature bond strength data for the above three primers are shown in Table 16. Included for comparison are average strength data for hydrolyzed Z-6040 siloxane primer bonds made in accordance with Bonding Procedure 13. It can be seen from the data that none of the epoxy primers produce bond strengths equivalent to bond strengths obtained with the hydrolyzed Z-6040 primer. Table 17 contains the formulations and procedures used to prepare adherends with the primers discussed.

Effect of Integrally Blending Siloxane Coupling Agents with Narmco 7343 Adhesive

Reports on experiments appear in the literature whereby siloxanes are added directly into the adhesive or polymeric binder.(1-3) These integral blends give increased bond strengths equivalent to bonds made with siloxane applied directly as primers to adherends or reinforcements. It has already been shown that the Dow-Corning Z-6020 and Z-6040 siloxanes greatly improve Narmco 7343 bond strength when employed as an adherend primer. A study was therefore conducted in which these two siloxanes were added to the adhesive to determine whether the priming operation could be eliminated. Bonds were made in accordance with Bonding Procedure 10, except siloxane was added to the adhesive after it had been premixed with the curing agent. The results of this study are shown in Table 18. Z-6020 siloxane, being an aliphatic amine, reacts with the 7343 immediately upon being added and causes the adhesive to become semi-gelled. The siloxane being reacted with the high (≈ 3000) molecular weight prepolymer before it is applied to the adherend is not free to migrate to the aluminum surface during the gelation period and therefore gives results which are equivalent to unprimed bonds. However, Z-6040 siloxane is an epoxy which reacts much slower with the 7343/7139 system, and causes no apparent reaction during mixing and layup. As a result, the Z-6040 is free to migrate from the adhesive to the adherend surface where it can react to form chemical bonds between the adherend and adhesive. This is confirmed by the obvious improvement in bonds made with Z-6040 integral blend over unprimed bonds.

TABLE 16
EFFECT OF EPOXY PRIMERS ON ROOM TEMPERATURE BOND STRENGTH

Set No.	Prime Used	RT Bell Peel Strength, pli				RT Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
217	X292	15	20	12	9	1920	2670	1110	32
218	X305	18	25	13	9	2120	2620	920	32
219	Epon 828/ Versamid 125 + Z-6040	57	60	53	9	2800	4000	1120	32
	Hydrolyzed Z-6040 (Procedure 13)	68	134	34	81	3122	4750	1460	448

N = number of specimens tested.

TABLE 17
ADHEREND PRIMERS USED WITH NARMCO 7343 ADHESIVE

Set No.	Name	Concentration	Solvent	Application	Cure
207 208 209 210	Epon 828 Versamid 125	50% } 1% 50% }	Toluene	Spray	1, 3, 7, 24 hr @ RT
217	Narmco X292 Shell Z	14 phr Shell Z to X292	None	Linen gauze wipe	20 hr @ RT
218	Narmco X305 Shell Z	13 phr Shell Z to X305	None	Linen gauze wipe	20 hr @ RT
219	Epon 828 Versamid 125 Dow Corning Z-6040	1 g 50/50 828/125 0.2 g Z-6040 98.8 g toluene	Toluene	Spray	20 hr @ RT

TABLE 18

ROOM TEMPERATURE STRENGTHS OF SILOXANE PRIMED AND
SILOXANE INTEGRAL BLEND BONDS

Set No.	Siloxane	Concentration, pph	Bell Peel Strength, psi				Shear Strength, psi			
			Avg	High	Low	N	avg	High	Low	N
211	None	--	44	67	33	18	1500	2680	990	48
213		--	138	148	119	12	2655	3710	1510	32
215		--	59	66	47	9	1340	1820	750	32
212	Z-6020	0.50 **	44	47	38	9	1440	1960	770	32
214	Z-6020	0.25 **	99	107	88	6	2920	3330	2190	16
215	Z-6040	-- *	97	108	84	9	2200	2980	1280	32
216	Z-6040	0.50 **								

* Siloxane applied as a primer on the adherend.

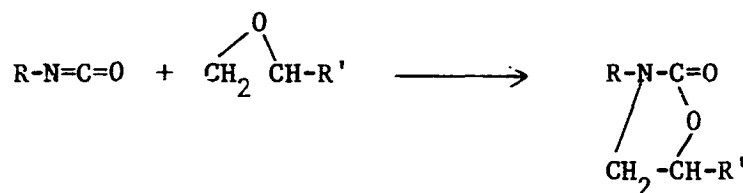
** Siloxane blended integrally with 7343 adhesive.

N = number of specimens tested.

Combined Effect of Z-6040 Siloxane/7343 Integral Blend with Hydrolyzed Z-6040 Siloxane Primer. - It was shown that Dow-Corning Z-6040 siloxane, improves bond strengths when used as an integral blend with the 7343 adhesive and that it also improves bond strengths when used as a primer on aluminum. A study was conducted wherein these two procedures were combined by priming the adherends with a 0.2-pph hydrolyzed Z-6040/methanol solution and by adding 1.0-phr of Z-6040 siloxane to the 7343 adhesive (Procedure 14).

Test results obtained from all bonds made by the above three procedures are shown in Table 19. The data indicate that the combined primer and integral blend produces higher room temperature bond strengths than does either one individually.

Shelf Life of Z-6040/7343 Blend. - A study was conducted to determine if Z-6040 siloxane can be premixed with 7343 adhesive without decreasing the shelf life of the adhesive. It is known that epoxies (i.e., the epoxy group of Z-6040) can react with urethanes, as shown below. The reaction is slow, however, and may not proceed at room temperature under the dry conditions present in the container.



For this study, a 2-lb container of Narmco 7343 was blended with 1.0-phr of Dow-Corning Z-6040 siloxane. This adhesive was used periodically to make nonprimed bonds which were then tested at room temperature. The bonds were made according to Bonding Procedure 10 except that the adhesive was neither heated nor degassed before it was mixed with the 7139 curing agent. Heat was avoided because it could have produced a reaction between the two blended materials.

Test data obtained are plotted in Figure 1. While some slight loss of strength may exist over a 12-week storage period, this strength loss is not significant, and apparently the 7343/Z-6040 blend can be stored for extended periods.

Effect of Humidity on Narmco 7343 Adhesive

During the first year's investigation, it was shown that humidity caused a very serious loss of bond strength, and that siloxane primers such as Dow-Corning Z-6020 and Z-6040 greatly improved bond strength and humid strength retention.

TABLE 19

EFFECT OF Z-6040 SILOXANE/7343 INTEGRAL BLEND WITH
HYDROLYZED Z-6040 SILOXANE PRIMER

Procedure No.	Z-6040 Hydrolyzed Primer, 0.2 pph	Z-6040 Integral Blend, 1.0 phr	Test Type	-320°F				Room Temperature				+200°F			
				Avg	High	Low	N	Avg	High	Low	N	Avg	High	Low	N
13	Yes	No	Ball peel	73	89	56	18	68	134	34	81	68.5	94	40	18
			Lap shear	8426	9200	5300	64	3122	4750	1460	448	1725	3000	625	64
--	No	Yes	Ball peel	73	87	55	9	128	176	100	27	92	112	68	9
			Lap shear	8750	9490	7950	31+1*	2667	3990	1290	96	1650	2230	1090	31
14	Yes	Yes	Ball peel	67	79	44	8	118	152	98	46	--	--	--	--
			Lap shear	7475**	--	6000	8+8*	3380	4840	2300	208	--	--	--	--

N = number of specimens tested.

* Metal Failure.

** Test average is low because of large number of metal failures.

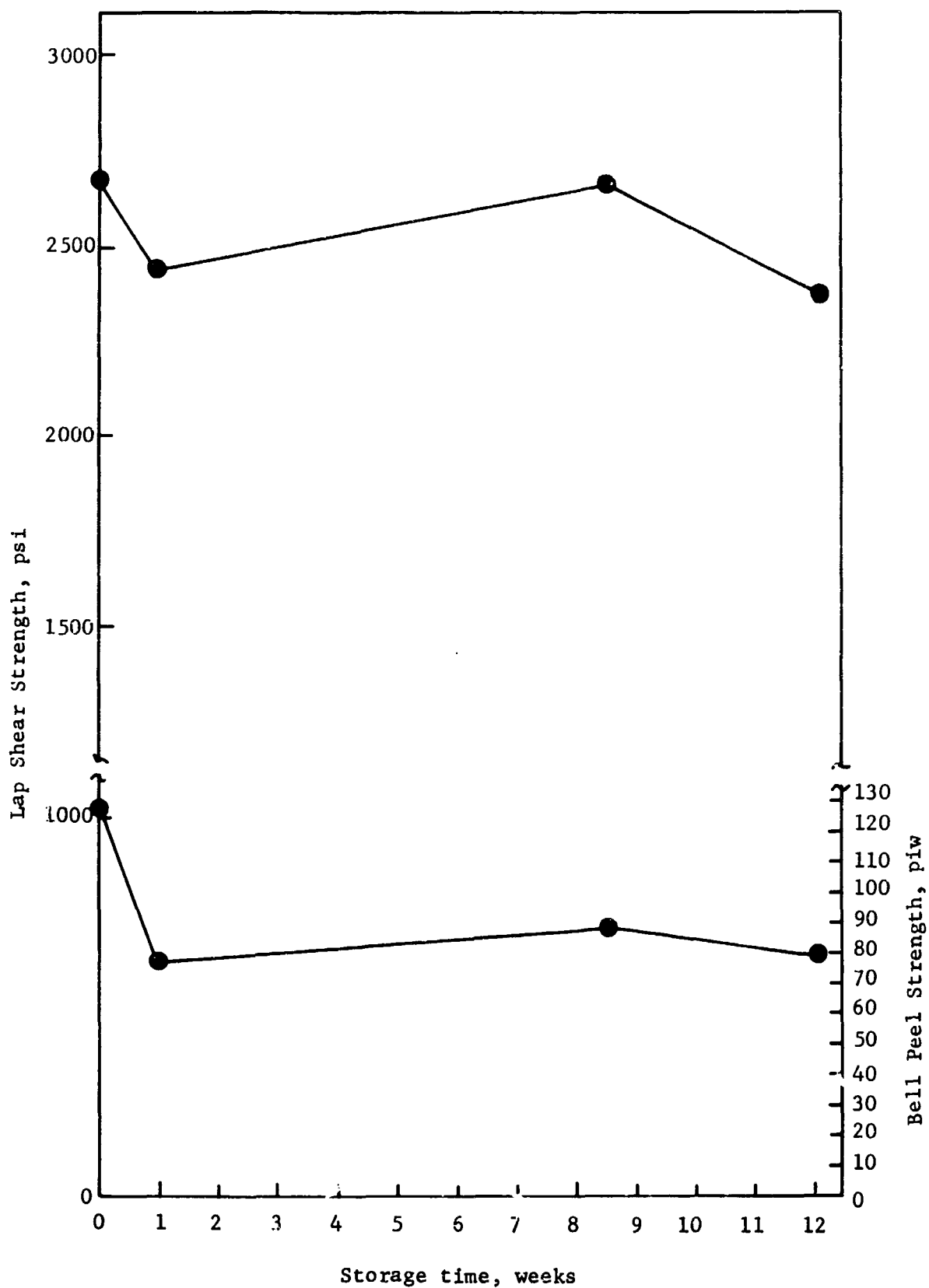


Figure 1. Effect of Storage Time of Uncatalyzed 1.0-phr Z-5040/7343 Integral Blend on Room Temperature Bond Strength

Extended Time Humid Storage Study. — Because no definite conclusions were reached as to the long-term effect of humidity during the first year, an 8-month humid storage study was conducted. During this study, bonds were stored in a humidity chamber over water controlled at 80°F to provide 100% RH humidity in the chamber.

Figures 2 through 7 compare exposure data obtained. The data show a general leveling off of bond strength after an initial serious loss of strength. They also show the primed bonds to be far superior to the nonprimed bonds, with the hydrolyzed Z-6040 siloxane primer being slightly better than the Z-6020 siloxane primer.

Specimen Dry Storage versus Ambient Storage. — A study was conducted to determine the effect on strengths of desiccant dry bag storage of bonds prior to test. Bonds were made in accordance with Bonding Procedures 8 (dry storage) and 10 (ambient storage). The data in Tables 20 through 22 compare the strengths at -320°F, room temperature, and +200°F show no marked change with ambient storage. However, lap shear strengths for bonds made according to Bonding Procedure 10 show a decrease of about 24% at room temperature, about 12% at -320°F, and about 26% at +200°F from bonds made by Bonding Procedure 8.

Another study was carried out to determine whether the observed strength degradation after the normal 8 days of ambient storage was produced by incomplete polymerization. A large set of nonprimed bonds was prepared and stored under dry conditions (0%-5% RH) for the normal 8-day period to assure a more complete cure. After this 8-day period, all specimens were removed from dry storage except one control set which was set aside for future comparison. Table 23 shows the strength data obtained for these ambient stored bonds tested 0, 1, 5, 8, and 12 days after dry storage removal. For comparison, the dry-stored control set was also tested on the twelfth day. Figure 8, derived from the data in Table 23, shows a steady decline in Bell peel and lap shear strengths with time. After 12 days of ambient storage, lap shear strengths declined 48%, and Bell peel strengths declined 16%. Because the control set strength data did not change during the 12-day period, it was concluded that the observed strength degradation is a function of ambient storage time.

Further studies were conducted with bonds premixed with various siloxanes and bonds utilizing a siloxane blended with the Narmco 7343 adhesive. The strength data obtained are shown in Tables 24 through 30. Table 31 shows the percent change in Bell peel and lap shear strengths at -320°F, room temperature, and +200°F for the various procedures used. All procedures showed a decrease in bond strength when stored under ambient conditions of 50%-60% RH at 70°-74°F, with the exception of -320°F lap shear bonds, which increased slightly. Furthermore, an integral blend of Dow-Corning Z-6040 siloxane and 7343 adhesive yielded smaller deviations in strength with ambient storage.

This study was expanded to also encompass the ambient storage performance of Z-6040 hydrolyzed siloxane primed/l-phr siloxane blended bonds. Table 32 lists the strengths of the primed and blended bonds after 0, 5, 10, and 28 days of ambient storage and 28 days of dry storage.

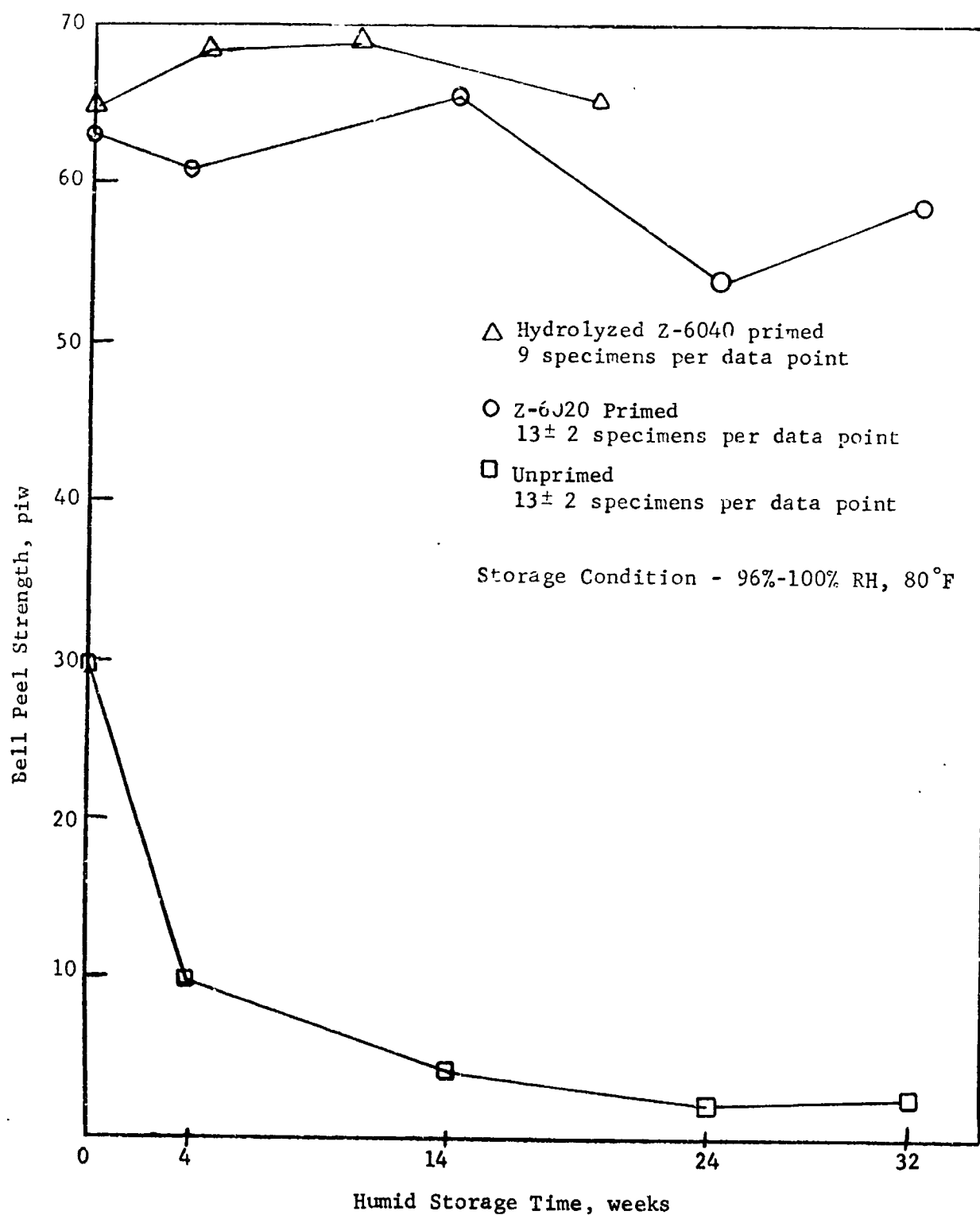


Figure 2. Effect of Humid Storage Time on Primed and Nonprimed -320°F Bell Peel Strength

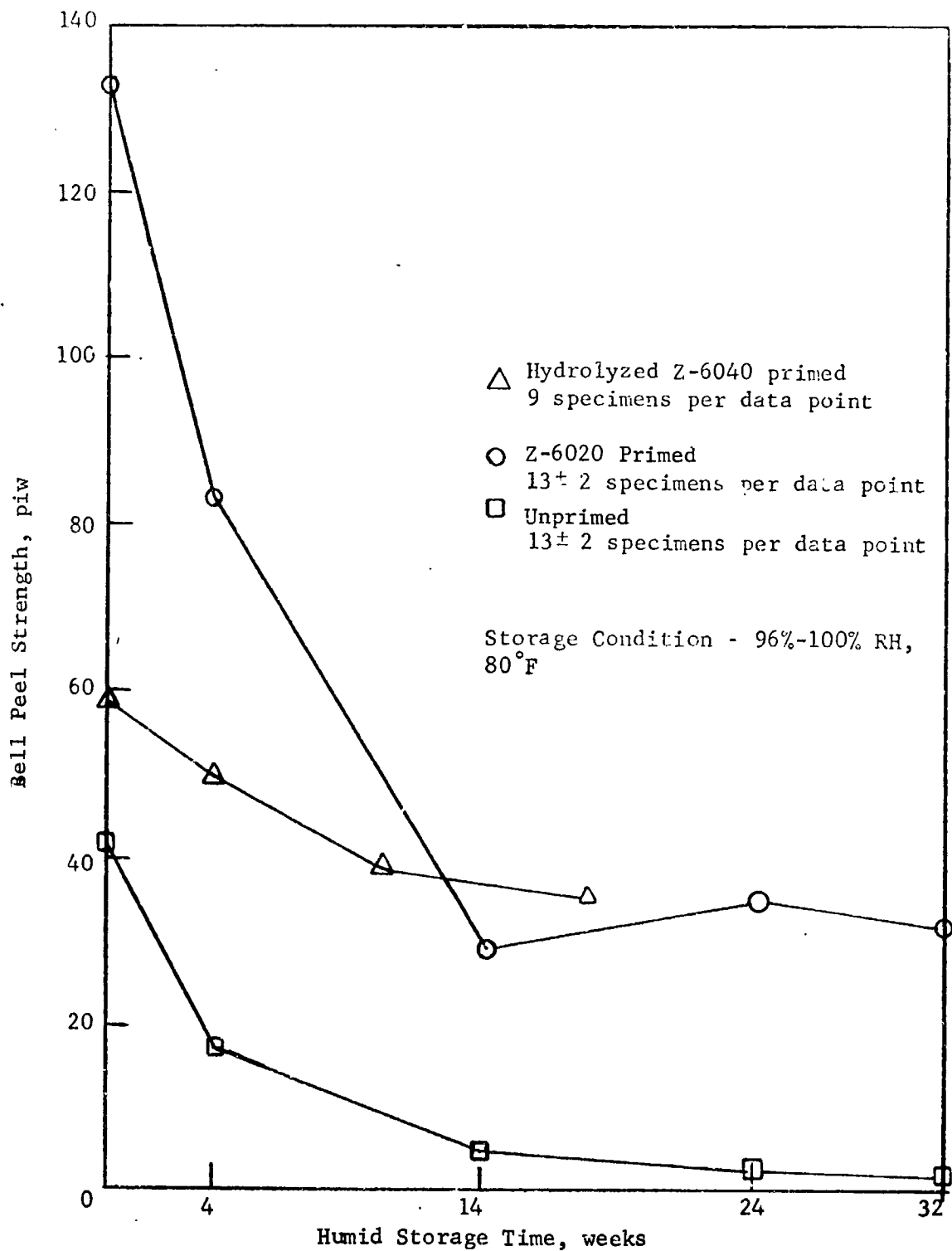


Figure 3. Effect of Humid Storage Time on Primed and Nonprimed Room Temperature Bell Peel Strength

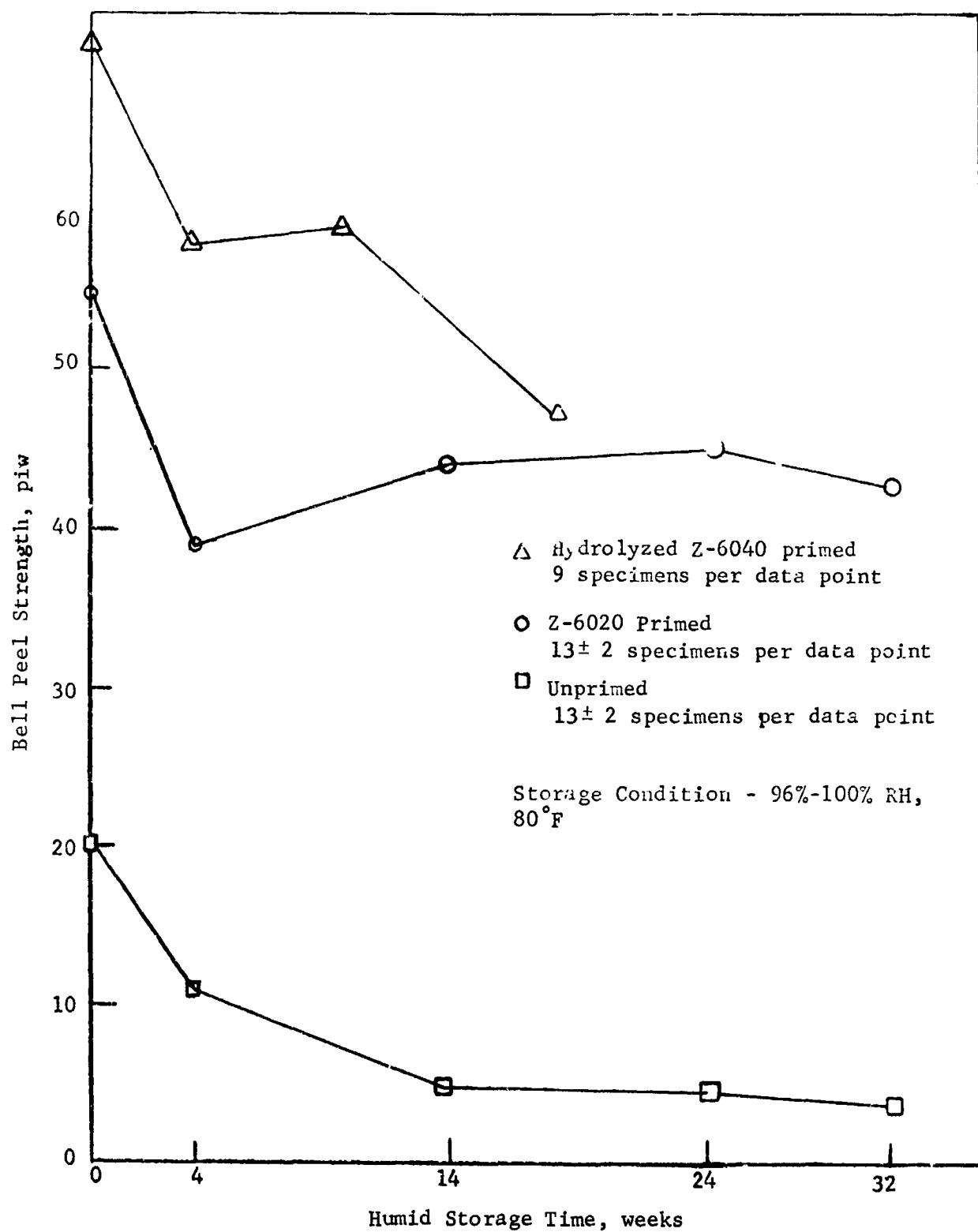
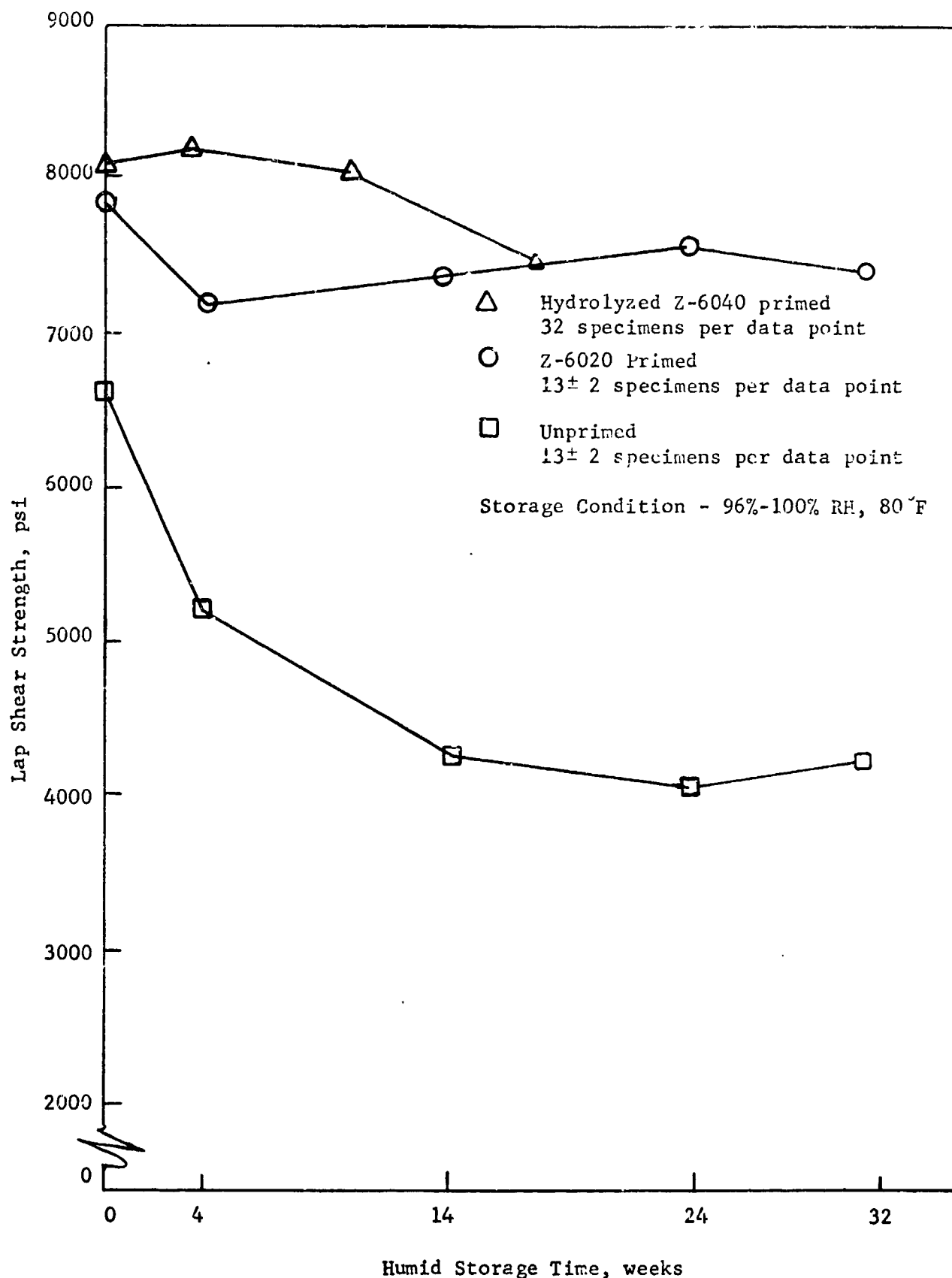


Figure 4. Effect of Humid Storage Time on Primed and Nonprimed +200°F Bell Peel Strength



Note: Value of 1128 psi for an individual specimen was eliminated from 4 week Z-6020 primed data point on the basis that the value was statistically improbable.

Figure 5. Effect of Humid Storage Time on Primed and Nonprimed -320°F Lap Shear Strength

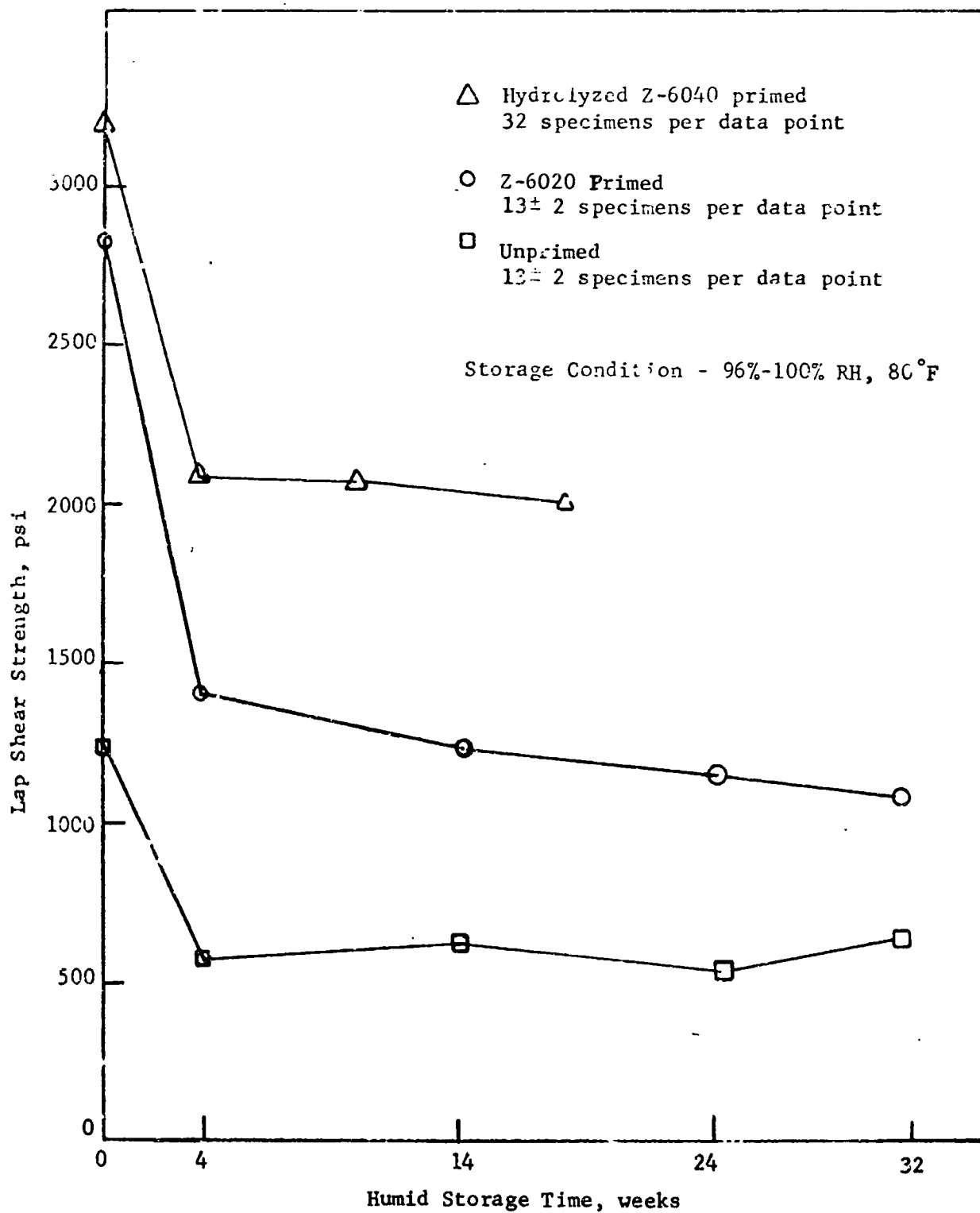


Figure 6. Effect of Humid Storage Time on Primed and Nonprimed Room Temperature Lap Shear Strength

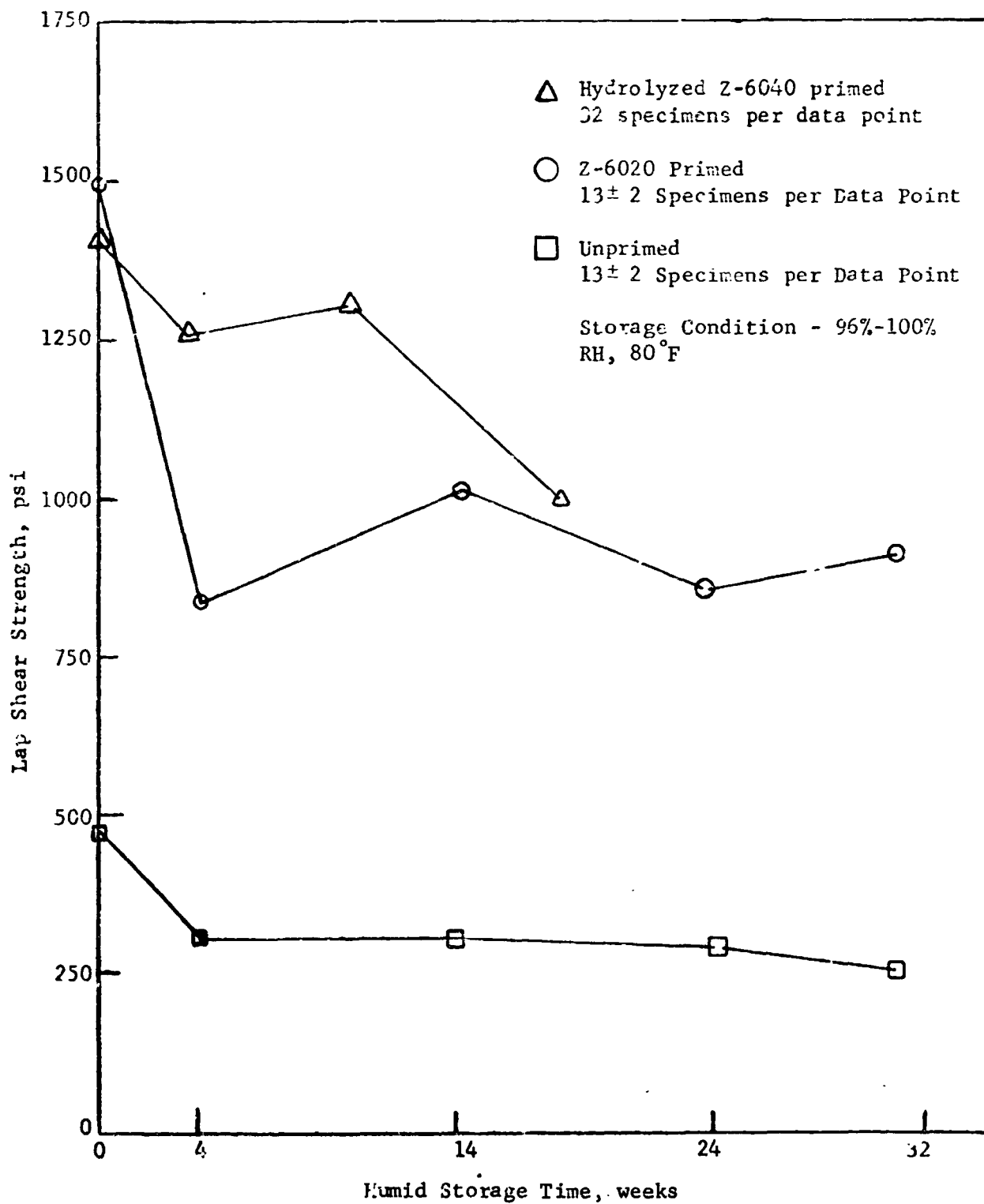


Figure 7. Effect of Humid Storage Time on Primed and Nonprimed +200°F Lap Shear Strength

TABLE 20
COMPARISON OF ROOM TEMPERATURE BOND STRENGTH FOR BONDS MADE BY
BONDING PROCEDURES 8 AND 10

Bonding Procedure	RT Bell Peel Strength, piw				RT Lap Shear Strength, psi			
	Set No.	Set Avg	High	Low	N	Set Avg	High	Low
8	240	48	59	37	36	2190	2740	1740
10	240	47	54	41	36	1682	1962	1336
8	250	40	49	34	36	2030	2730	1360
10	250	40	46	31	36	1500	1880	1020

N = number of specimens tested.

TABLE 21

COMPARISON OF -320°F BOND STRENGTH FOR BONDS MADE BY
BONDING PROCEDURES 8 AND 10

Bonding Procedure	Set No.	-320 Bell Peel Strength, piw				-320 Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
8	249	33	53	17	16	7210	8800	5800	32
10	249	37	49	25	16	6650	8450	4900	32

N = number of specimens tested.

TABLE 22

COMPARISON OF +200°F BOND STRENGTH FOR BONDS MADE BY
BONDING PROCEDURES 8 AND 10

Bonding Procedure	Set No.	+200 Bell Peel Strength, piw				+200 Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
8	249	31	40	23	16	439	544	256	32
10	249	20	29	13	16	323	452	206	32

N = number of specimens tested.

TABLE 23

EFFECT OF AMBIENT AND DRY STORAGE TIME ON ROOM TEMPERATURE NONPRIMED BOND STRENGTHS

Cure Cycle	Ambient Storage Time, days	Dry Storage Time, days	Set No.	Bell Peel Strength, psi				Lap Shear Strength, psi			
				Set Avg	High	Low	N	Set Avg	High	Low	N
16 hr @ RT + 24 hr @ 160°F + 8 day @ RT (Dry) ↓	0	0	281-2	48	53	44	9	2163	2650	1520	32
	1	0	281-2	47	53	36	9	2080	2520	1430	32
	5	0	281-2	45	4	4	9	1600	2200	700	32
	8	0	281-2	43	46	38	9	1340	1560	1080	32
	12	0	281-2	40	46	35	9	1240	1540	930	32
	0	12	281-2	47	51	43	9	2160	2940	1520	32

N = number of specimens tested.

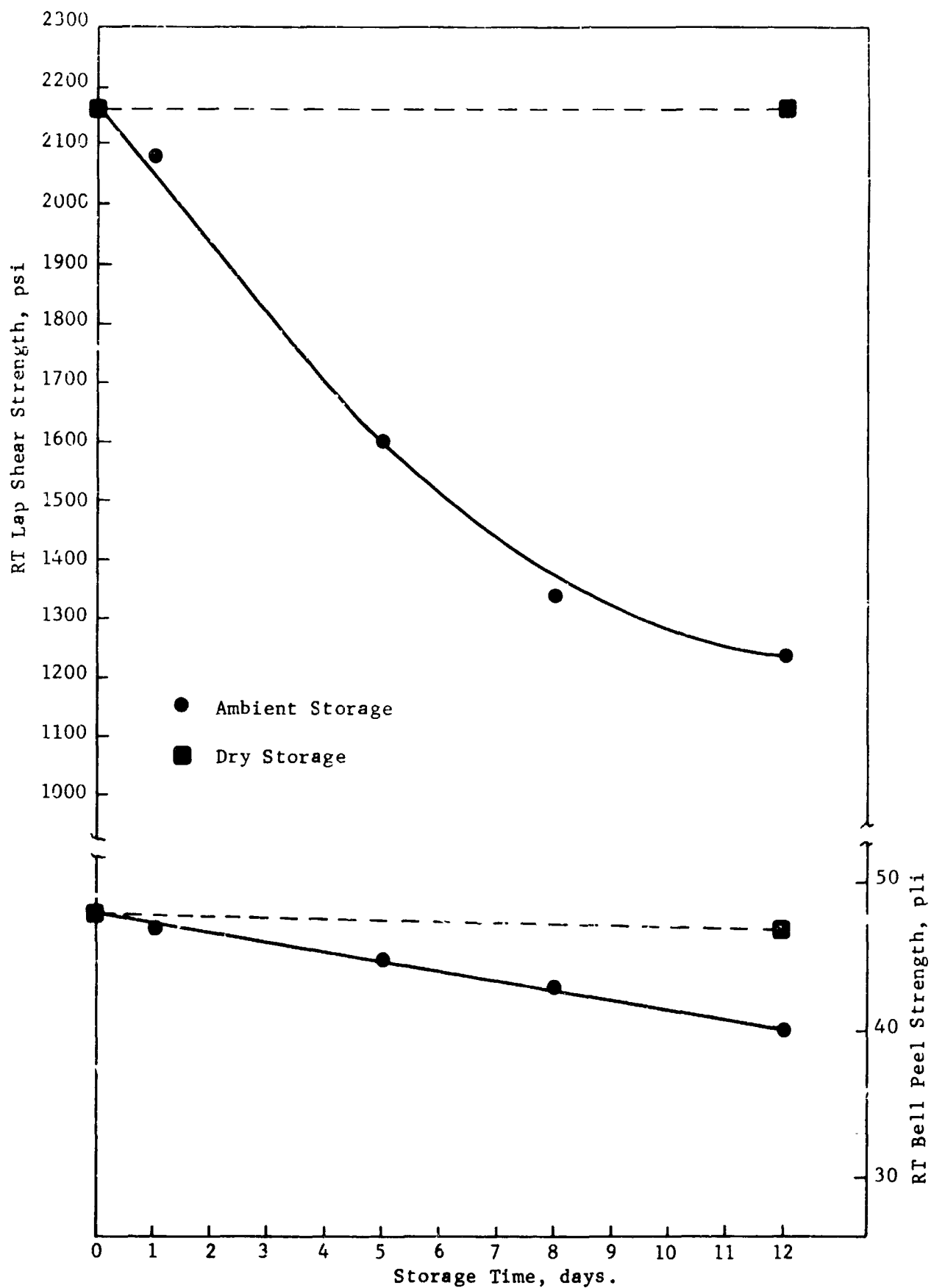


Figure 8. Effect of Ambient and Dry Storage Time on Non-Primed Room Temperature Bond Strengths

TABLE 24

COMPARISON OF ROOM TEMPERATURE Z-6020 SILOXANE PRIMED BOND STRENGTH
STORED UNDER DRY AND AMBIENT CONDITIONS

Storage Conditions	Set No.	Bell Peel Strength, piw				Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
Dry	273	40	162	122	36	3582	4620	2320	64
Ambient	273	131	150	120	36	2510	3820	1820	64

N = number of specimens tested.

TABLE 25

COMPARISON OF -320°F Z-6040 SILOXANE INTEGRAL BLEND BOND STRENGTH
STORED UNDER DRY AND AMBIENT CONDITIONS

Storage Conditions	Set No.	Bell Peel Strength, piw				Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
Dry	284-5	75	85	68	9	8590	9220	7520	32
Ambient	284-5	73	87	55	9	8750	9490	7950	32

N = number of specimens tested.

TABLE 26

COMPARISON OF ROOM TEMPERATURE Z-6040/7343 SILOXANE INTEGRAL BLEND BOND
STRENGTH STORED UNDER DRY AND AMBIENT CONDITIONS

Storage Conditions	Set No.	Bell Peel Strength, piw				Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
Dry	284-5	110	125	100	9	3270	4120	1780	32
Ambient	284-5	109	117	100	9	2880	3780	1700	32

N = number of specimens tested.

TABLE 27

COMPARISON OF +200°F Z-6040 SILOXANE INTEGRAL BLEND BOND STRENGTH
STORED UNDER DRY AND AMBIENT CONDITIONS

Storage Conditions	Set No.	Bell Peel Strength, piw				Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
Dry	284-5	94	122	73	9	1670	2420	891	32
Ambient	284-5	92	112	68	9	1650	2230	1090	31

N = number of specimens tested.

TABLE 28

COMPARISON OF -320°F Z-6040 HYDROLYZED SILOXANE PRIMED BOND STRENGTH
STORED UNDER DRY AND AMBIENT CONDITIONS

Storage Conditions	Set No.	Bell Peel Strength, piw				Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
Dry	286-7	82	89	70	9	8610	9200	7670	32
Ambient	285-7	81	89	73	9	8670	9200	7990	32

N = number of specimens tested.

TABLE 29

COMPARISON OF ROOM TEMPERATURE Z-6040 HYDROLYZED SILOXANE PRIMED BOND
STRENGTH STORED UNDER DRY AND AMBIENT CONDITIONS

Storage Conditions	Set No.	Bell Peel Strength, piw				Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
Dry	286-7	94	139	55	9	3700	4750	2420	31
Ambient	286-7	83	130	52	9	3420	4460	2260	32

N = number of specimens tested.

TABLE 30
COMPARISON OF +200°F Z-6040 HYDROLYZED SILOXANE PRIMED BOND STRENGTH
STORED UNDER DRY AND AMBIENT CONDITIONS

Storage Conditions	Set No.	Bell Peel Strength, piw				Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
Dry	286-7	72	109	35	9	2470	3690	1410	32
Ambient	286-7	67	94	40	9	2050	3000	1400	32

N = number of specimens tested.

TABLE 31

COMPARISON OF BONDING PROCEDURES WITH % CHANGE
FROM DRY STORAGE CONDITIONS AT ROOM TEMPERATURE, +200°F, AND -320°F

Set No.	Bonding Procedure	% Change from Dry Storage Strength					
		RT		-320°F		+200°F	
		Bell Peel	Lap Shear	Bell Peel	Lap Shear	Bell Peel	Lap Shear
273	Primed with 0.2 pph Dow-Corning Z-6020 Siloxane (Procedure 9)	-7%	-29%	--	-	--	--
284	1.0 phr Dow-Corning Z-6040 Siloxane added to adhesive	-1%	-12%	-2.6%	+2%	-1%	-1%
285							
286	Primed 0.2 pph Dow-Corning Z-6040 Hydrolyzed Siloxane	-11.5%	-8%	-1.2%	+0.7%	-7%	-16%

TABLE 32

EFFECT OF AMBIENT AND DRY STORAGE ON ROOM TEMPERATURE
Z-6040 HYDROLYZED PRIMED PLUS Z-6040 INTEGRAL BLENDED BOND STRENGTHS

Cure Cycle	Ambient Storage Time, days	Dry Storage Time, days	Set No.	Bell Peel Strength, psi			Lap Shear Strength, psi		
				Set Avg	High	Low	Set Avg	High	Low
16 hr @ RT 24 hr @ 160°F 8 days @ RT (Dry) ↓ ↓ ↓	0	0	341,2,3	109	132	57	3660	4840	2590
	5	0	341,2,3	111	120	100	3540	4410	2030
	10	0	341,2,3	120	145	113	3500	4800	2680
	28	0	341,2,3	108	131	63	3615	4650	2500
	0	28	341,2,3	125	133	110	3800	4600	3250

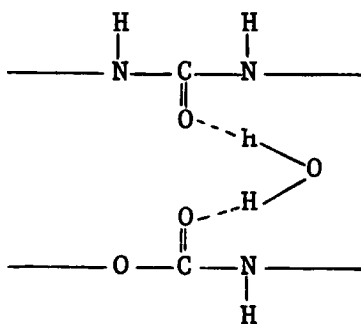
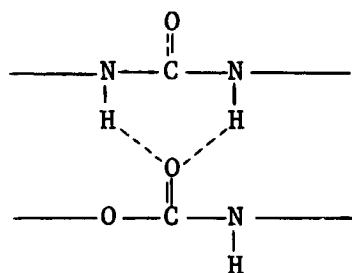
N = number of specimens tested.

Figures 9 and 10 compare the strength retention performance of the bonds to the earlier nonprimed bonds. Both nonprimed Bell peel and lap shear strengths declined steadily throughout the storage period. However, the Z-6040 hydrolyzed siloxane primed/1-phr Z-6040 integral blend Bell peel and lap shear exhibited excellent strength retention for 28 days of storage.

During the preparation of the above bonds, an additional set was made and coated with Apco 1510 to determine if this coating would further contribute to strength retention. Table 33 shows the bond strengths obtained for 0, 5, and 10 days of ambient storage. Figure 11 is a comparison of the strength retention of the coated and noncoated bonds. The coating did not appear to enhance the strength retention of stored, primed, and blended bonds.

Reversible Effect of Water Adsorption. — A significant result of this study was that about 70% of the initial nonprimed bond strength was regained when bonds which were exposed to high humidity were subsequently dried (see Table 34). This finding is in agreement with results reported in the literature,⁽⁴⁾ which show that water adsorbed by a polyether type polyurethane produces two effects: reversible plasticization and an irreversible degradation of the urea and urethane bonds. Apparently the observed bond strength recovery was due to the reversible plasticization effect, while the lack of complete recovery may have been caused by the irreversible degradation.

The plasticization effect is apparently the result of water forming hydrogen bonds with polar carbonyl groups in the adhesive. This theory is supported by additional work at Narmco which showed that 1.9% water was adsorbed by a 7343 adhesive specimen when it was boiled for 5 days. This 1.9% water adsorption is equivalent to 1 water adsorbed per 1.7 carbonyl groups and is very close to the theoretical value of 1 water per 2.0 carbonyl groups, as shown below.



Hydrogen bonds present in dry adhesive

—— Normal Chemical Bond
 ---- Hydrogen Bond

Hydrogen bonds with water

(1 water per 2 carbonyls)

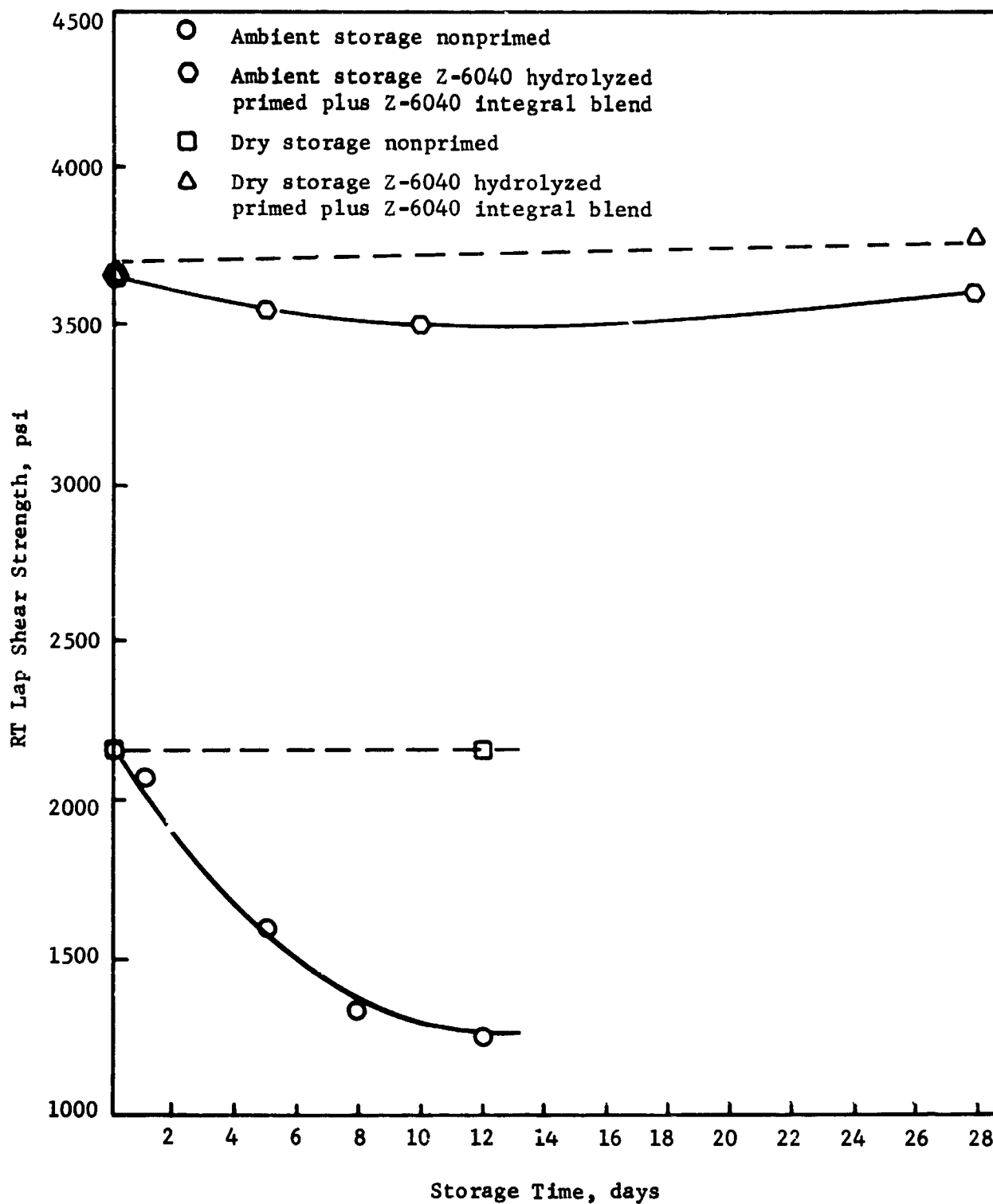


Figure 9. Effect of Ambient and Dry Storage Time on Nonprimed and Z-6040 Hydrolyzed Primed Plus Z-6040 Integral Blend Room Temperature Lap Shear Strengths

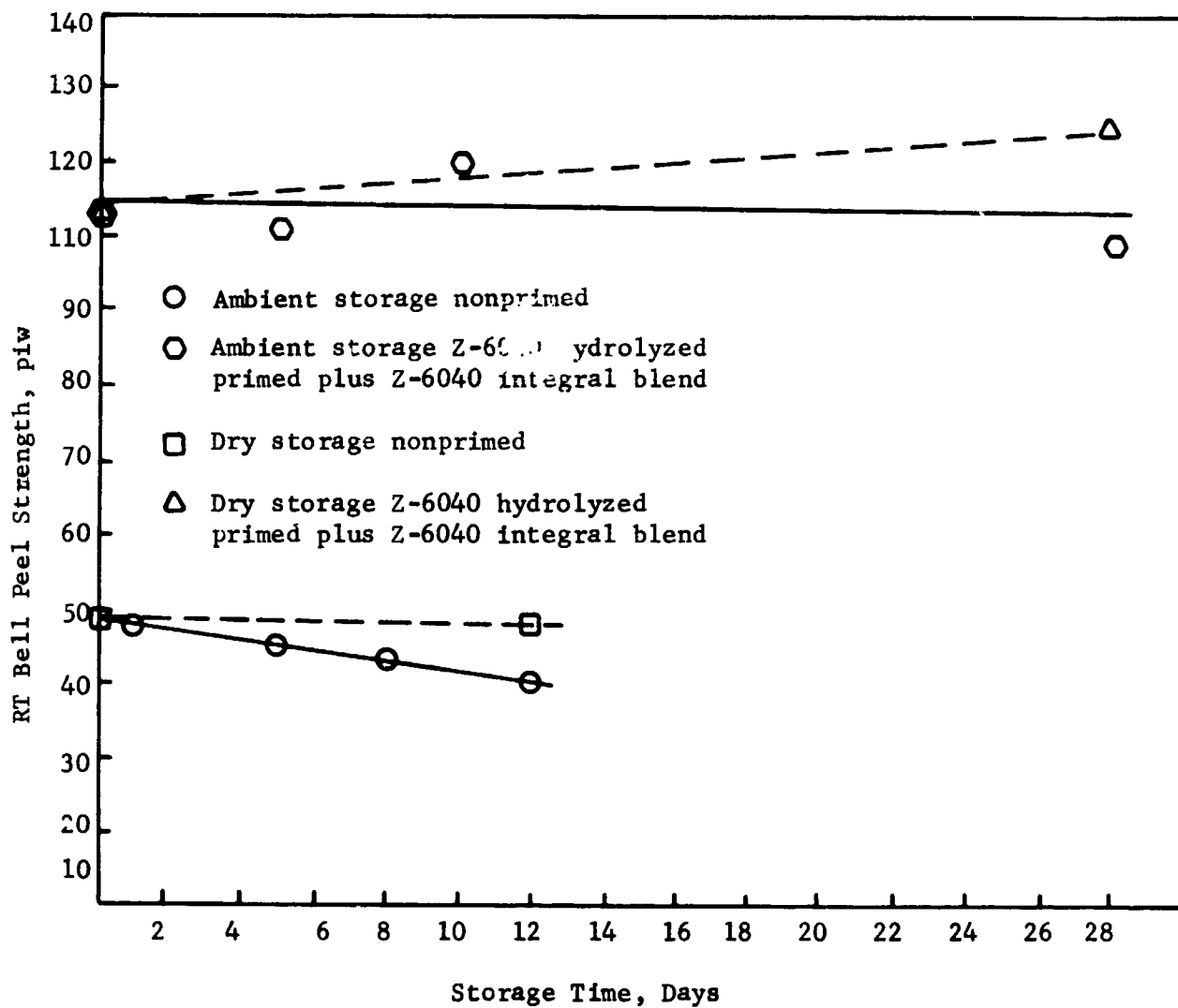


Figure 10. Effect of Ambient and Dry Storage Time on Nonprimed and Z-6040 Hydrolyzed Primed Plus Z-6040 Integral Blend Room Temperature Bell Peel Strengths

TABLE 33
EFFECT OF AMBIENT STORAGE ON ROOM TEMPERATURE
BOND STRENGTH OF Z-6040 HYDROLYZED PLUS Z-6040 INTEGRAL BLENDED BONDS
COATED WITH APCO 1510 COATING FOR URETHANE ADHESIVES

Cure Cycle	Ambient Storage Time, Days	Dry Storage Time, Days	Set No.	Bell Peel Strength, piw			Lap Shear Strength, psi		
				Set Avg	High	Low	Set Avg	High	Low
16 hr @ RT	0	0	341,2,3	109	132	59	3780	5000	1400
24 hr @ 160°F				114	126	103	3350	4350	2230
8 days @ RT (Dry)				119	136	100	3570	4400	2560
	10	0	341,2,3						

N = number of specimens tested.

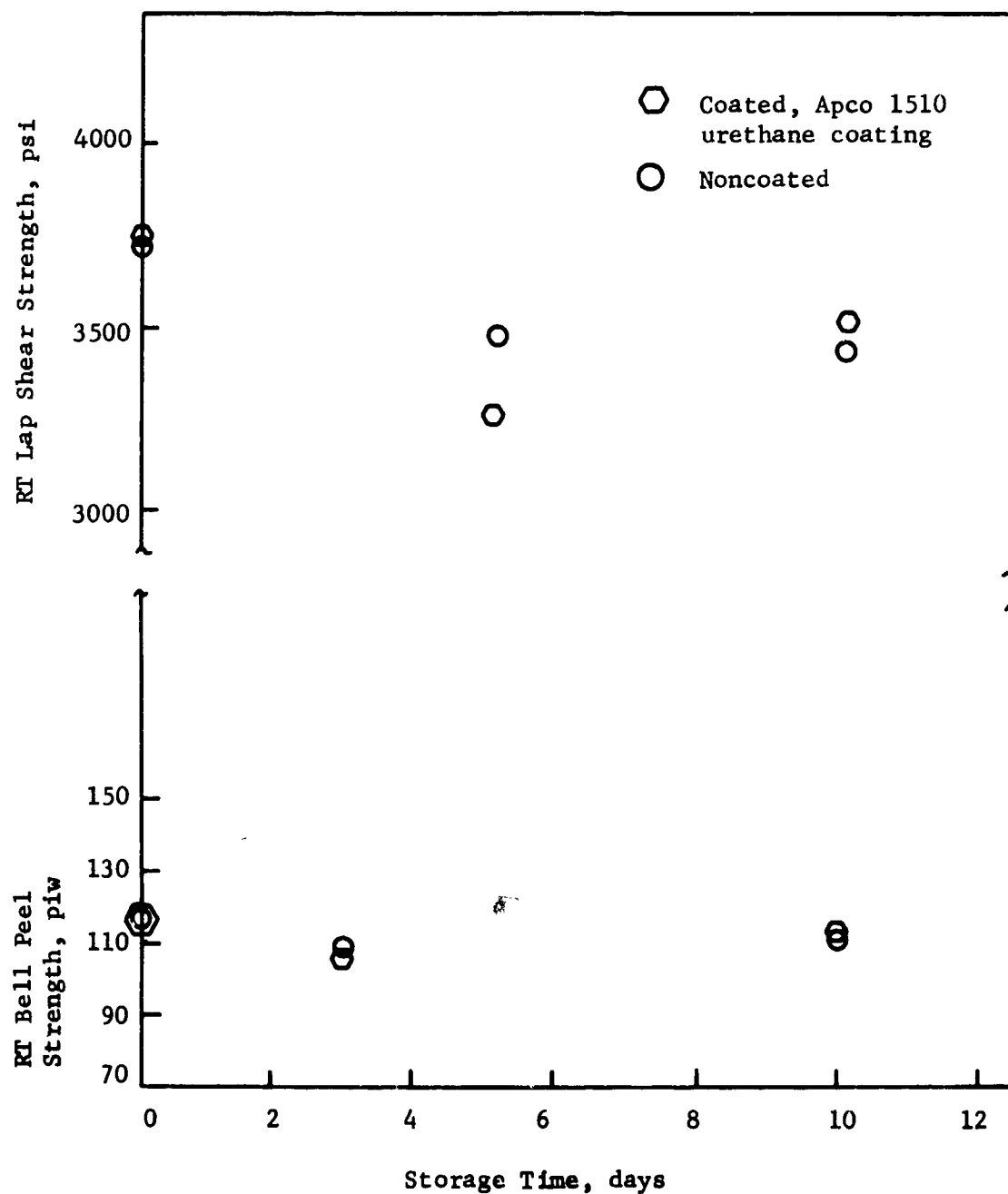


Figure 11. Effect of Apco 1510 Urethane Coating on Z-6040 Hydrolyzed Primed Plus Z-6040 Integral Blended Room Temperature Lap Shear and Bell Peel Strengths

TABLE 34

EFFECT OF DRYING BONDS STORED AT 100% RELATIVE HUMIDITY

Set No.	Storage Conditions	Lap Shear, psi				Bell Peel, piw			
		Avg	High	Low	N	Avg	High	Low	N
283	Initial	2280	2810	1840	32	50	54	47	9
283	4 weeks @ \approx 100% RH	810	1150	560	32	7	12	3	9
283	4 weeks @ \approx 100% RH followed by 1 week @ \approx 0% RH	1570	1800	1300	32	21	24	17	9

N = number of specimens tested.

Hardness measurements conducted on the 5-day water boil specimen showed that it changed from a Shore A hardness of 94 to a hardness of 75 after the water boil exposure; at the end of 10 days of storage over Drierite desiccant, the specimen lost 99% of the water pickup during the water boil exposure, with Shore A hardness recovering to 83.

Effect of Various Formulations on Narmco 7343/7139 Adhesive System

Effect of Various Curing Agent Concentrations on Bond Strength. - A series of bonds was made using Bonding Procedure 10, except curing agent concentrations, varying between 9.0 and 13.0 phr were used. This study was a duplication of an earlier study, which gave a low confidence level due to the lack of a sufficient number of specimens.

The data obtained from the new study are shown in Tables 35 and 36 and Figure 12. However, the -320°F Bell peel autographic recordings, which previously were erratic for bonds made with less than 12 phr of curing agent, no longer displayed this characteristic.

The data indicate that a curing agent concentration between 10.5 and 13.0 phr gives equivalent room temperature results. However, from the limited -320°F strength data obtained, it appears that low temperature strengths are improved with lower concentrations. On the basis of these findings, it appears that curing agent concentrations between 10.5 and 11.5 are near optimum.

Effect of Water Concentrations on Room Temperature Bond Strength. - Because humidity has been shown to be detrimental to cured bonds, several studies were conducted to determine the effect of any water that might be adsorbed by the adhesive at the time of layup. This water can act as a co-curing agent with the Narmco 7139 curing agent, and can change the final molecular structure of the adhesive as shown by the following reactions:

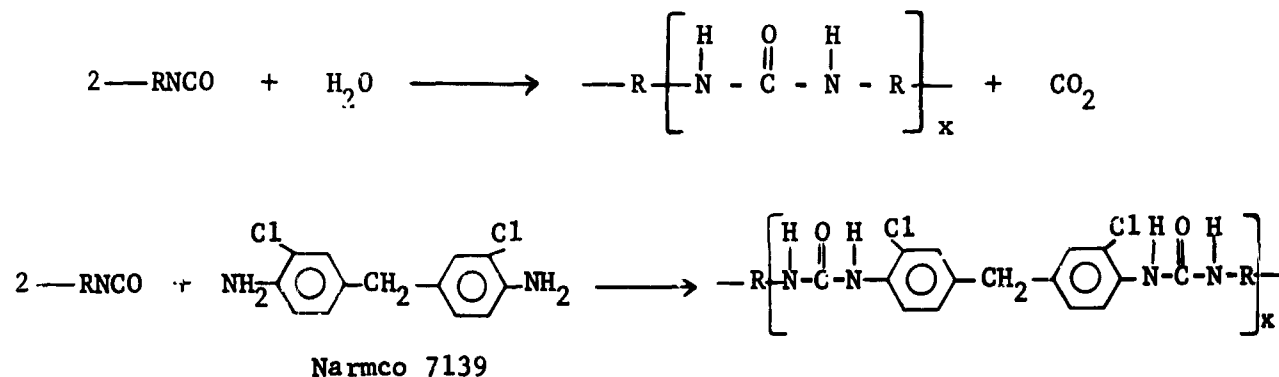


TABLE 35

EFFECT OF NARMCO 7139 CURING AGENT CONCENTRATION ON BELL PEEL STRENGTH

Curing Agent Concentration, phr	RT Bell Peel Strength, piw				-320°F Bell Peel Strength, piw			
	Avg	High	Low	N	Avg	High	Low	N
9.0	44	54	37	9	53	70	46	9
10.0	50	60	44	9	50	60	37	9
10.5	56	62	50	9	--	--	--	--
11.0	46	50	43	9	--	--	--	--
11.5	51	58	46	9	--	--	--	--
12.0	41	45	39	9	--	--	--	--
12.5	40	46	36	9	29	44	17	9
13.0	43	48	39	9	20	27	10	9

N = number of specimens tested.

TABLE 36

EFFECT OF NARMCO 7139 CURING AGENT CONCENTRATION ON LAP SHEAR STRENGTH

Curing Agent Concentration, phr	KR Lap Shear Strength, psi				-320°F Lap Shear Strength, psi			
	Avg	High	Low	N	Avg	High	Low	N
9.0	1140	1500	820	36	8600	9100	7200	18 + 18*
10.0	1330	1760	840	32	8480	9000	5750	25 + 7*
10.5	1690	2200	1400	32	--	--	--	--
11.0	1580	1980	1200	32	--	--	--	--
11.5	1590	1920	1410	24	--	--	--	--
12.0	1540	1880	1290	32	--	--	--	--
12.5	1550	1960	1310	32	7570	8860	4250	32
13.0	1640	2020	1260	32	5960	8000	4750	32

N = number of specimens tested.

* Metal Failure.

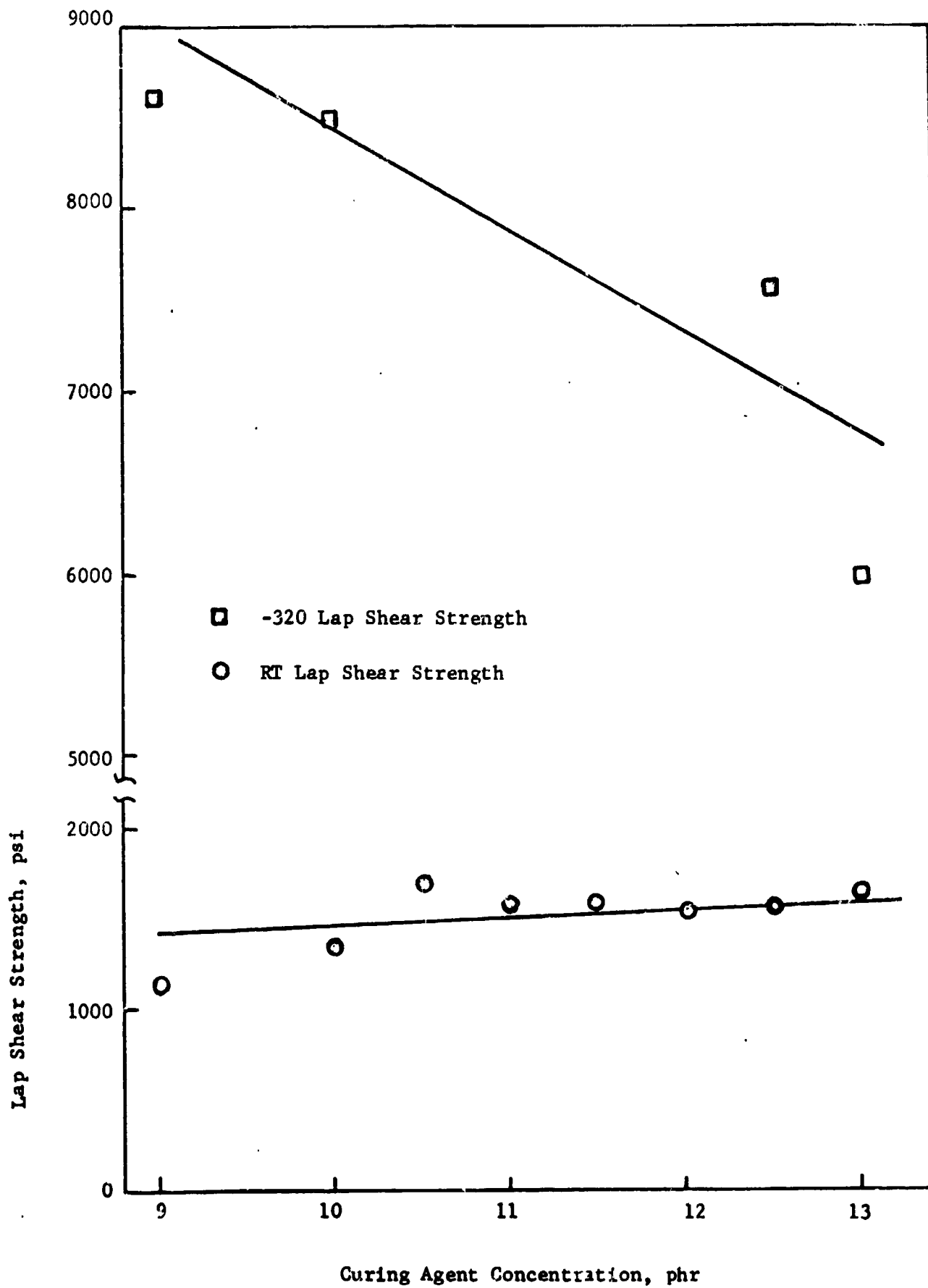


Figure 12. Effect of 7139 Curing Agent Concentration on Lap Shear Strength

Table 37 contains results obtained from a study in which bonds made by Bonding Procedure 10 were allowed to remain open for various lengths of time after the adhesive was applied to the adherend. Because the adhesive is solvent-free, it is probable that the only important effect of this open period is water adsorption from the atmosphere. Viscosity changes due to adhesive advancement is considered negligible because of the long time required to gel the system at ambient temperatures.

The data show an apparent trend toward lower bond strength with increased open time. However, because of the wide range of values within a given data point, and because all of the data point averages fall within the range typical for 7343 adhesive, the validity of the results is open to question. Nevertheless, the data indicate that long open times are not beneficial.

In two other studies, specimens were made according to Bonding Procedure 10, except that various amounts of water were added to the uncured catalyzed adhesive prior to application. In one study, the 7139 concentration was held constant at 12.5 phr (93.7% of stoichiometry), and in the other study, the combined 7139 and water stoichiometry totaled 93.7%.

Experiments showed that adhesive formulated with water as the only curing agent does not become tack-free with the normal (24 hours at 160°F) postcure. Therefore, bonds made with water as the only curing agent were subjected to 24-hour exposure at 200°F to ensure complete cure at the time of test. Bonds made with a water/7139 curing agent received the normal 160°F cure.

Results of testing bonds at room temperature are shown in Tables 38 and 39. Evidently, water in moderate concentrations does not appreciably affect bond strength; however, as the ratio of water to 7139 increases, bond strength does drop off slightly. Also, examination of failed bondlines showed appreciable foaming, due to the liberation of carbon dioxide gas from the water cure.

These studies tended to reaffirm the previous observation that humidity affects the adhesive-adherend interface of cured bonds, but that it does not appreciably affect the bulk of the cured adhesive by reacting with free NCO groups.

Effect of a Polyol Co-Curing Agent on Room Temperature Bond Strength. — In an effort to improve the adhesion of Narmco 7343, the incorporation of a polyol co-curing agent was investigated. Reagan⁽⁵⁾ described an improvement in the peel strengths of thin polyurethane films on aluminum obtained when free hydroxyl groups were present in the cured polymer.

With this in mind, the 7139 amine curing agent being used and a urethane grade triol, Pluracol TP440,* were combined to form co-curing agents. The amine curing agent (7139) has been shown to react faster than the polyol curing agent selected for this study. Therefore, the co-curing agent used in excess of stoichiometry will have the desired free hydroxyl groups remaining in the cured polymer.

* Product of Wyandotte Chemicals Corporation, Wyandotte, Michigan

TABLE 37

EFFECT OF OPEN TIME OF SPREAD ADHESIVE ON ROOM TEMPERATURE BOND STRENGTH

Open Time, hr	Set No.	RT Bell Peel Strength, piw					RT Lap Shear Strength, psi				
		Set Avg (Avg of 6)	Combined Avg	High	Low	N	Set Avg (Avg of 6)	Combined Avg	High	Low	N
Initial	190*	40.5	45	52	34	12	1680	1690	2100	1260	32
	191**	49					1700				
1/2	190*	29	33	46	24	12	1540	1358	1780	990	32
	191**	37					1175				
1	190*	16	29.5	46	14	12	1278	1132	1450	1020	32
	191**	43					1107				
2	190*	15.5	27.5	43	12	12	1200	1090	1565	745	32
	191**	39.5					980				

N = number of specimens tested.

* 70% relative humidity.

** 62% relative humidity.

TABLE 38

EFFECT OF WATER CONCENTRATION ON BOND STRENGTH FOR BONDS MADE
USING CONSTANT TOTAL STOICHIOMETRY

Set No.	Water Concentration, phr (% Stoichiometry)	7139 Concentration, phr (% Stoichiometry)	Postcure Cycle	RT Lap Shear Strength, psi				RT Bell Peel Strength, piw			
				Avg	High	Low	N	Avg	High	Low	N
194	0.84 (93.5%)	0 (0)	24 hr @ 200°F	182	254	10	21	6	7		9
195	0.28 (31.2%)	8.35 (62.5%)	24 hr @ 160°F	845	1269	430	32	46	54	38	9
196	0.085 (9.4%)	11.25 (84.3%)	24 hr @ 160°F	1414	1788	920	32	49	54	45	9
197	0.025 (2.8%)	12.1 (90.8%)	24 hr @ 160°F	1275	1600	790	32	40	49	34	9

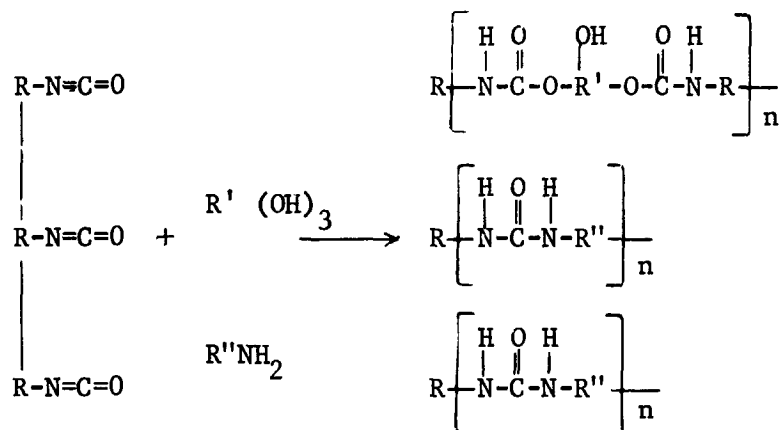
N = number of specimens tested.

TABLE 39

EFFECT OF WATER CONCENTRATION ON BOND STRENGTH FOR BONDS MADE
USING CONSTANT AMINE CURING AGENT CONCENTRATION

Set No.	Water Concentration, phr (% Stoichiometry)	7139 Concentration, phr (% Stoichiometry)	RT Lap Shear Strength, psi				RT Bell Peel Strength, piw			
			Avg	High	Low	N	Avg	High	Low	N
198	0.20 (22.2%)	12.5 (93.7%)	1390	1818	1114	32	39	41	37	9
199	0.075 (8.3%)	12.5 (93.7%)	1330	1891	990	32	38	48	31	9
200	0.025 (2.8%)	12.5 (93.7%)	1546	1877	1356	32	34	37	28	9

N = number of specimens tested.



The curing agent concentrations and room temperature bond strengths obtained are shown in Table 40. In all cases, the room temperature Bell peel and lap shear strengths were lower than the average strengths obtained using the standard Bonding Procedure 10. Because the Shore A hardness for all polyol specimens ranged from 81-91 as compared with the hardness of normal specimens of 89-93, the properties of the adhesive were not believed to be significantly altered. Because all failures were in the adhesion mode, it was concluded that the use of a polyol co-curing agent with Narmco adhesive 7343 for these applications does not enhance its adhesive properties.

Aluminum and Aluminum Oxide Fillers. - A number of bonds were made using adhesive which contained aluminum (MD105) or aluminum oxide (B&A) fillers. Bond strength test results are shown in Table 41. While some improvement may have ensued from inclusion of 20 phr of aluminum powder with 1% Z-6040 siloxane coupling agent, the improvement was not sufficient to justify further work.

Toluene Diisocyanate Concentrations. - Toluene diisocyanate (TDI) is present in Narmco 7343 prepolymer in an amount of about 0.7 phr; however, much of this TDI is removed when the prepolymer is vacuum-degassed prior to the addition of the curing agent.* TDI, a difunctional isocyanate, forms a very hard and brittle polymer when cured by Narmco 7139 curing agent, which is much harder than 7343. Because of this increase in hardness, additional TDI, if added to the 7343 prepolymer, should effect the hardness and flexibility of the cured polymer.

A study was conducted to determine the effect of TDI concentration on bond strengths. Adhesive batches were made wherein 0.25, 1.0, and 5.0 phr of TDI (100% 2,4-isomer) were added to the degassed prepolymer immediately before addition of the Narmco 7139 curing agent. The added TDI increased the Shore A hardness of the material from the normal 91 (for no TDI) to 94.5 for adhesive made with 5 phr of added TDI. Strength data for bonds made with

* TDI removal is evidenced by strong TDI odor in vacuum trap, however, the collected residue has not been quantitatively analyzed for TDI.

TABLE 40

EFFECT OF POLYOL CO-CURING AGENT ON ROOM TEMPERATURE BOND STRENGTH

Set No.	% Stoichiometry 7139	% Stoichiometry Polyol TP440	% Total Stoichiometry	RT Bell Peel Strength, piw				RT Lap Shear Strength, psi			
				Set Avg	High	Low	N	Set Avg	High	Low	N
252	30	80	110	18	20	17	6	425	730	266	13
253	30	90	120	26	28	23	6	210	380	92	14
254	30	100	130	19	21	15	6	87	121	70	16
255	60	50	110	35	38	33	6	1430	1760	1120	16
256	60	60	120	33	35	30	6	1080	1275	160	16
257	60	70	130	24	34	17	6	675	890	160	16
258	80	30	110	36	38	35	6	1240	1810	670	16
259	80	40	120	30	32	27	6	1225	1440	960	16
260	80	50	130	33	34	32	6	1120	1280	880	16
261	95	15	110	40	41	38	6	1590	1730	1340	16
262	95	25	120	42	44	40	6	926	1340	730	16
263	95	35	130	45	51	44	6	924	1130	750	16

N = number of specimens tested.

TABLE 41

EFFECT OF FILLERS ON ROOM TEMPERATURE BOND STRENGTH

Set No.	1 phr Z-6040 Integral Blend	Filler and Concentration	Lap Shear Strength, psi				Bell Peel Strength, piw			
			Avg	High	Low	N	Avg	High	Low	N
291	No	None	1770	2280	1520	32	56	62	47	9
292	No	Al ₂ O ₃ -20 phr	1160	1260	1080	16	57	60	52	9
293	No	Al ₂ O ₃ -50 phr	875	980	730	16	66	68	64	9
294	No	Al - 20 phr	1470	1820	740	16	64	70	59	9
295	No	Al - 50 phr	1830	2160	1580	16	72	76	67	9
302	Yes	None	2540	3720	1290	32	153	176	135	9
303	Yes	Al ₂ O ₃ -20 phr	2120	2800	1710	32	93	101	87	9
304	Yes	Al ₂ O ₃ -50 phr	1780	2020	1520	32	99	106	94	9
305	Yes	Al - 20 phr	3100	3500	2200	52	99	105	93	9
306	Yes	Al - 50 phr	2950	3730	1960	32	100	108	90	9

N = number of specimens tested.

0.25 and 1.0 phr are shown in Table 42. The adhesive made with 5.0 phr of excess TDI gelled during mixing and, therefore, bonds of this concentration could not be made. The test results do not show a significant improvement in bond strength with added TDI.

TABLE 42
EFFECT OF TOLUENE DIISOCYANATE CONCENTRATION
ON ROOM TEMPERATURE BOND STRENGTH

Set No.	TDI Concentration, phr	Lap Shear Strength, psi				Bell Peel Strength, piw			
		Avg	High	Low	N	Avg	High	Low	N
296	0	1995	2780	1520	32	61	67	52	9
297	0.25	1660	2360	1180	24	48	54	39	9
298	1.0	2660	2560	1980	32	49	53	45	9

N = number of specimens tested.

Effect of Processing Changes on Narmco 7343/7139 Adhesive System

Effect of Various Mixing Procedures on Room Temperature Bond Strength. -- Data reported in Annual Summary Report No. 1 indicated that bonds made with adhesive mixed in a high shear (Waring) blender gave improved results over bonds made with adhesive that was mixed mechanically at low speeds. This work also indicated that heating and degassing of the 7343 and 7139 adhesive components may not be beneficial. A new study was completed in which various mixing procedures were used with both heated and ambient temperature adhesive components.

Specimens were made according to Bonding Procedure 10, except that adhesive batches were mixed by hand for 1 minute, followed by 4 minutes in a mechanical mixer or four passes through a hand-operated emulsifier. The procedures were repeated four times to include the various combinations of ambient and degassed prepolymer with ambient (powdered) and molten curing agent.

The void content of the adhesive was determined by density measurements of cured castings made from the adhesive batches. Microscopic examination of these coatings showed the nominal bubble size to be about 0.5 mil in diameter.

The data obtained in the study are shown in Table 43. The data indicated that the type of mixer (see Figure 13) controls the void content of the adhesive and the void content is related to the bond strength (see Figure 14). The mixing procedure which gave the lowest void content (i.e., the hand emulsifier) gave the highest bond strengths.

The data also appeared to indicate that better bond strengths are obtained if one adhesive component is heated while the other is at ambient conditions; however, if both components are heated or both are ambient conditions, strengths are lower.

Effect of a Nondegassed Adhesive Procedure on Bond Strength. - The preceding observation that bond strength is improved when one adhesive component is not heated and degassed led to a repeat study in an attempt to substantiate these findings. Tables 44 and 45 are a comparison of the strength obtained for bonds made without heating and degassing the 7343 adhesive component with the strength of bonds made by normal procedure (No. 10). While the data indicated slight improvement of -320°F strength from the ambient temperature adhesive, the heating and degassing operation is still recommended for ease of mixing with the molten curing agent and ease of application of the adhesive to the adherend.

Effect of a Scrim Cloth Carrier on Room Temperature Bond Strength. - Glass scrim cloth carriers are commonly used to control bondline thickness. The carrier also acts as a reinforcement for the adhesive and at the same time reduces the flexibility of the bondline. However, it is recognized that a glass scrim cloth could be unsatisfactory for certain cryogenic applications because of the danger of wicking liquid oxygen. With this possible limitation in mind, a study was made with a glass carrier to determine the effects of closer bondline control. A 112-112 scrim cloth (112 glass cloth, 112 finish) was used in place of the glass beads normally used to control bondline thickness. Test results for nonprimed bonds are shown in Table 46. Indications are that while the scrim cloth had little effect on lap shear strength, it greatly reduced the data spread (standard deviation), presumably because of closer bondline thickness control.

TABLE 43

EFFECT OF VARIOUS MIXING PROCEDURES ON ROOM TEMPERATURE BOND STRENGTH

Set No.	Mixing Procedure			Void Content, Volume %	Lap Shear Strength, psi				Bell Peel Strength, piw			
	Mixer	7343 Prepolymer	7139 Curing Agent		Avg	High	Low	N	Avg	High	Low	N
223	Hobart Slow ¹	Degassed ⁵	Molten ⁶	0.95	1390	1640	1070	32	39	42	35	9
220	Hobart Fast ²	↓	↓	35.0	890	1300	570	32	27	29	24	9
221	Emulsifier ³	↓	↓	0.80	1378	1880	880	32	45	49	42	9
222	Blender ⁴	↓	↓	17.6	1215	1520	810	32	42	47	36	9
235	Hobart Slow ¹	Degassed ⁵	Powdered ⁷	4.8	1460	1890	1170	32	42	47	36	9
232	Hobart Fast ²	↓	↓	35.4	1240	1580	930	32	30	34	28	9
233	Emulsifier ³	↓	↓	2.8	1540	1840	1250	32	45	47	41	9
234	Blender ⁴	↓	↓	18.7	1460	2080	980	32	47	51	44	9
231	Hobart Slow ¹	Ambient	Molten ⁶	10.6	1580	1840	1330	32	45	51	38	9
228	Hobart Fast ²	↓	↓	38.4	1180	1470	710	32	26	29	24	9
229	Emulsifier ³	↓	↓	4.6	1565	1800	1250	32	44	50	38	9
230	Blender ⁴	↓	↓	19.4	1600	1930	1300	32	47	49	44	9
227	Hobart Slow ¹	Ambient	Powdered ⁷	19.7	1108	1580	680	32	36	40	32	9
224	Hobart Fast ²	↓	↓	34.0	1100	1420	640	32	38	41	35	9
225	Emulsifier ³	↓	↓	9.5	1182	1620	760	32	46	50	41	9
226	Blender ⁴	↓	↓	14.6	1138	1600	750	32	41	52	36	9

1 Normal procedure. See Experimental Section, 1.0 rps.

2 4.0 rps

3 Hand operated, orifice type (Matheson Scientific #51520-30); adhesive passed through four times.

4 Waring blender, heavy duty, low speed.

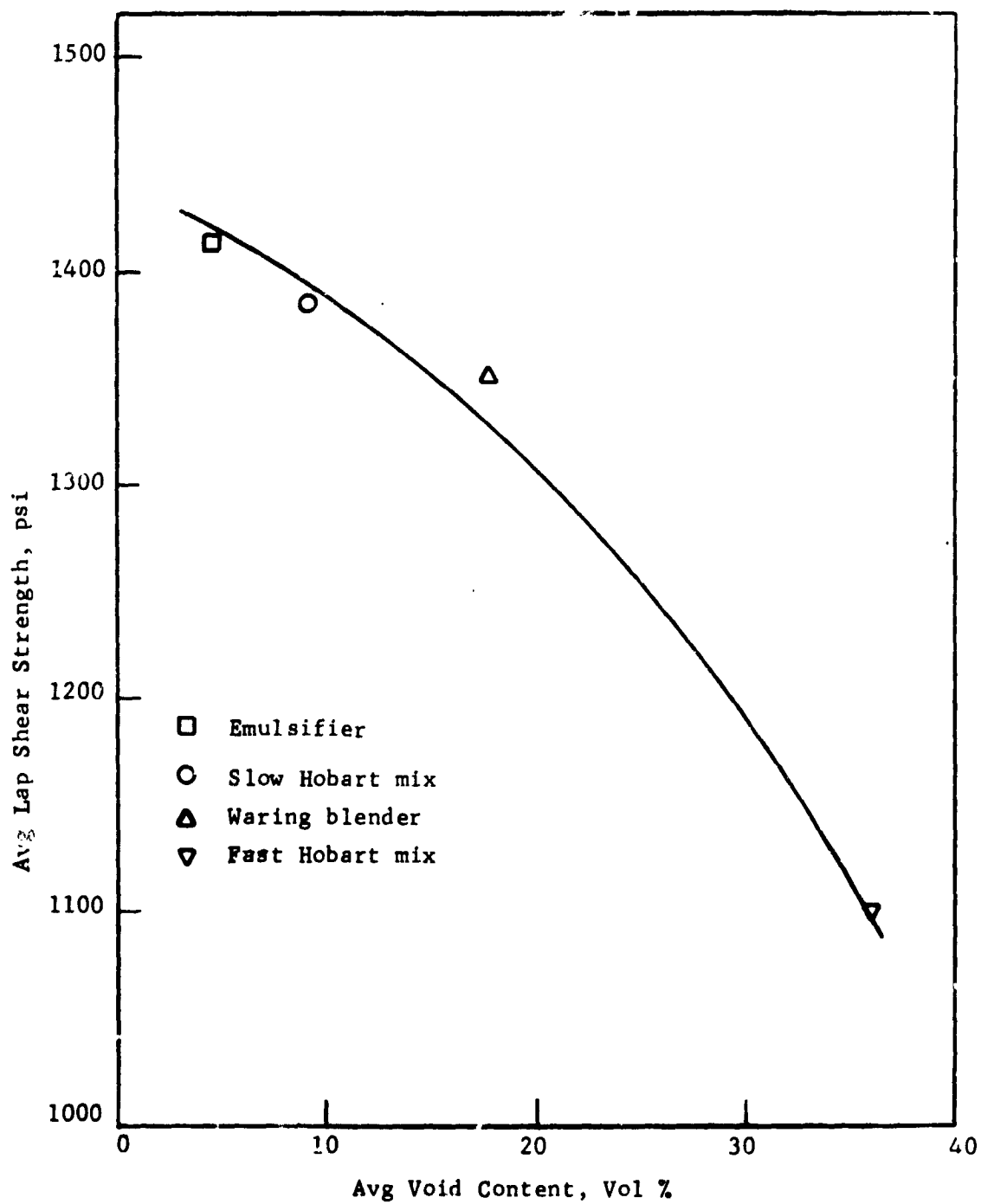
5 Normal procedure. See Experimental Section.

6 Normal procedure. See Experimental Section.

7 250 mesh.



Figure 13. Mechanical Mixers. From left to right,
Hobart Model N50 eccentric rotary mixer;
hand-operated orifice type emulsifier;
and Waring blender



Note: 128 specimens per data point.

Figure 14. Effect of Void Content on Room Temperature Lap Shear Strength

TABLE 44

COMPARISON OF DEGASSED AND NON-DEGASSED PROCEDURES ON ROOM TEMPERATURE BOND STRENGTH

Set No.	Prepolymer Preparation	RT Bell Peel Strength, piw				RT Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
223	Heated and Degassed ↑	39	42	35	9	1390	1640	1070	32
243		30	33	25	9	1400	1700	1130	32
245		30	34	28	9	1630	1900	1320	32
247		50	52	49	9	1900	2270	720	32
	Avg of Sets →	37			36	1580			128
231	Ambient and not Degassed ↑	45	51	38	9	1580	1840	1330	32
244		26	31	22	9	1130	1960	720	32
246		21	25	15	9	1290	1790	724	32
248		62	66	57	9	1690	2470	745	32
	Avg of Sets →	39			36	1422			128

N = number of specimens tested.

TABLE 45

COMPARISON OF DEGASSED AND NONDEGASSED PROCEDURES ON -320°F BOND STRENGTH

Set No.	Prepolymer Preparation	-320 Bell Peel Strength, piw				-320 Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
243	Heated and Degassed	38	60	11	9	7090	8650	4240	32
245									
247									
244	Ambient and not Degassed	51	83	19	9	8110	9320 (Failed Aluminum)	6740	32
246									
248									

N = number of specimens tested.

TABLE 46

EFFECT OF 112-112 SCRIM CLOTH ON NONPRIMED
ROOM TEMPERATURE BOND STRENGTH

Set No.	Procedure	Bell Peel Strength, piw				Lap Shear Strength, psi				
		Avg	High	Low	N	Avg	High	Low	N	σ
301	Glass Beads	48	52	45	9	2100	2480	900	32	300
301	Scrim Cloth	67	72	63	9	1846	2024	1650	32	95

N = number of specimens tested.

$$\sigma = \text{Standard deviation} = \sqrt{\frac{\sum (\bar{X} - X)^2}{n-1}}$$

Effect of an Adherend Alkaline Cleaner on Room Temperature Bond Strength.-

A study was conducted to determine whether or not the observed minor variations in the luster of 2024-T6 clad aluminum adherend surfaces after the sodium dichromate etch treatment, was contributing to some variation in bond strengths. The adherend panels were subjected to a standard alkaline cleaner to ensure complete cleansing of the aluminum to give greater uniformity in the etch treatment. The composition of the alkaline cleaner was 3 oz/gal trisodium phosphate and 3 oz/gal sodium carbonate.

A large set of room temperature nonprimed bonds was prepared and immersed in the alkaline cleaner for 1, 2, and 3 minutes at 140°-158°F prior to the standard 10 minute sodium dichromate etch treatment. Table 47 compares the room temperature bond strengths obtained for the three time periods used. The data showed no significant change in bond strengths nor did they show that the alkaline treatment yields more uniform bonds. It was concluded that the use of an alkaline cleaner for adherend preparation is not necessary for the 7343 adhesive system.

Room Temperature Strength of Bonds Prepared in Accordance with a Procedure Suggested by the Contracting Agency. - In response to a Contracting Agency request, a special bonding procedure and cure cycle was compared to the bonding procedure currently being used (Procedure 10). The special procedure is described in Table 48. Room temperature test data for bonds prepared in accordance with this procedure are shown in Table 49.

The average strengths obtained appeared to be about equal to the average strength usually obtained with normal Bonding Procedure 10.

TABLE 47
EFFECT OF AN ADHEREND ALKALINE CLEANER ON ROOM TEMPERATURE BOND STRENGTH

Adherend Preparation	Set No.	RT Bell Peel Strength, piw				RT Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
Normal 10 min, $\text{Na}_2\text{Cr}_2\text{O}_7$ etch	307	48	50	44	9	1960	2360	1070	32
1 min alkaline cleaner and rinse, $\text{Na}_2\text{Cr}_2\text{O}_7$ etch	307	50	53	47	9	1940	2160	1060	32
2 min alkaline cleaner and rinse, $\text{Na}_2\text{Cr}_2\text{O}_7$ etch	307	50	55	47	9	2000	2260	1760	32
3 min alkaline cleaner and rinse, $\text{Na}_2\text{Cr}_2\text{O}_7$ etch	307	54	59	50	9	1880	2320	1200	32

N = number of specimens tested

TABLE 48
COMPARISON OF DIFFERENCE BETWEEN THE CONTRACTING AGENCY'S
SUGGESTED CURE CYCLE AND BONDING PROCEDURE 10

	Suggested Bonding Procedure	Bonding Procedure 10
1	11.0 phr of Narmco 7139 curing agent	12.5 phr of Narmco 7139 curing agent
2	Panels open for 20 minutes between applying adhesive and uniting faying surfaces	Faying surfaces united within 2 or 3 minutes after applying adhesive
3	Cure cycle: 2 days @ RT then 6 hours at 140°F then 7 days at RT	Cure cycle: 1 day @ RT then 24 hours at 160°F then ~7 days at RT

TABLE 49

ROOM TEMPERATURE STRENGTH OF BONDS PREPARED IN ACCORDANCE WITH A
PROCEDURE SUGGESTED BY THE CONTRACTING AGENCY

Cure Cycle	Set No.	RT Bell Peel Strength, piw				RT Lap Shear Strength, psi			
		Set Avg	High	Low	N	Set Avg	High	Low	N
2 days @ RT 6 hrs @ 140°F 7 days @ RT	241	43	46	40	9	1490	1950	1240	24
2 days @ RT 6 hrs @ 140°F 14 days @ RT	241	46	52	43	9	1330	1520	1160	24
1 day @ RT 24 hrs @ 160°F ~7 days @ RT	Bond Procedure #10 *	44	67	25	153	1693	2780	720	416

* Bonding Procedure 10 data taken from Appendix A in this report.

N = number of specimens tested.

Effect of Various 140°F Postcure Cycles on Room Temperature Bond Strength.-

In conjunction with the above study, another study was conducted to determine whether or not room temperature bond strengths are improved by using a 140°F postcure cycle, and whether or not 140°F postcures in combination with various room temperature cures is the factor responsible for the observed improvement in bond strengths reported by others.

Eight sets of bonded peel and lap shear specimens were made in accordance with Bonding Procedure 10, except that the postcure cycle was 6 hours at 140°F instead of 24 hours at 160°F. In addition, each set had a different room temperature cure (prior to postcure) of 1, 2, or 3 days, and the period between layup and testing was varied between 4 and 24 days. The specific total cure cycle for each set is shown in Table 50. Test results, also shown in Table 50, indicate that Set 201 produced both Bell peel and lap shear strengths about 20% higher than bonds produced by Bonding Procedure 10. A similar improvement in average lap shear strength is noted for Set 206. The average strengths for all of the remaining bond sets are about equivalent to bonds made using Bonding Procedure 10. It is interesting that the cure cycle used in the preparation of Set 201 is similar to the established Bonding Procedure 10, with the exception of the 140°F postcure portion.

Effect of Time between Mixing and Layup on Room Temperature Bond Strength.-

A series of bonds was made in accordance with Bonding Procedure 10; however, the catalyzed adhesive was allowed to stand in the mixing container for various times before application. The test results, shown in Table 51, gave indication that the optimum application time may be 30 to 60 minutes after mixing. Variations in Bell peel strengths are believed to be caused by wide variation in bondline thickness produced by spreading and extremely viscous adhesive. The viscosity increase is caused primarily by cooling (from the mixing temperature of 160°F to room temperature). Average Bell peel bondline thicknesses varied from 8.2 mils (normal) for panels spread initially to 14.9 mils for panels spread at the end of 2 hours.

Effect of Blends of Polyurethane Adhesives

A study was conducted wherein blends of polyurethane adhesives similar to Narmco 7343 adhesive were used to make bonds. Test results obtained with bonds made from these blends, using Bonding Procedure 14, are shown in Tables 52 and 53. Room temperature lap shear strength was greatly improved with some of the adhesives and there was little or no sacrifice in other bond strengths measured. These data can be seen more clearly in Figure 15, where prepolymer blend composition is compared with bond strength from Table 52.

TABLE 50

EFFECT OF VARIOUS 140°F POSTCURE CYCLES ON
ROOM TEMPERATURE BOND STRENGTH

Set No.	Cure Cycle	RT-Bell Peel Strength, piw				RT Lap Shear Strength, psi			
		Avg	High	Low	N	Avg	High	Low	N
201	0 days @ RT + 6 hr* @ 140°F + 7 days @ RT	37	43	33	9	1410	1720	1160	32
201	1 day* @ RT + 6 hr @ 140°F + 6 days @ RT	53	58	50	9	1540	1800	1260	32
202	2 days** @ RT + 6 hr @ 140°F + 5 days @ RT	39	43	35	9	1198	1489	969	32
202	3 days** @ RT + 6 hr @ 140°F + 4 days @ RT	39	43	33	9	1061	1422	777	32
205	0 days @ RT 6 hr* @ 140°F 24 days @ RT	33	36	28	9	1040	1260	560	32
205	1 day* @ RT 6 hr @ 140°F 23 days @ RT	38	41	34	9	1180	1510	760	32
206	2 days** @ RT 6 hr @ 140°F 23 days @ RT	40	46	37	9	1520	1820	1210	32
206	3 days** @ RT 6 hr @ 140°F 23 days @ RT	40	42	35	9	1334	1650	940	32

N = number of specimens tested.

* Cured in vacuum bag.

** First 16 hours only in vacuum bag.

TABLE 51

EFFECT OF TIME BETWEEN MIXING AND LAYUP OF NARMCO 7343 ADHESIVE ON BOND STRENGTH

Time in Mix Pot, hr	Set No.	RT Bell Peel Strength, piw					RT Lap Shear Strength, psi				
		Set Avg	Combined Avg	High	Low	N	Set Avg (Avg of 6)	Combined Avg	High	Low	N
Initial	192	47*	47.5	50	43	12	1082	1150	1380	665	32
	193	48*					1218				
1/2	192	63*	60	69	47	12	1180	1338	1704	965	32
	193	57.7*					1495				
1	192	59**	55	63	44	9	1468	1420	1574	1168	32
	193	53*					1372				
2	192	62**	53	67	45	9	1025	972	1462	691	32
	193	48**					920				

N = number of specimens tested.

* Average of 6 specimens.

** Average of 3 specimens.

TABLE 52
EFFECT OF NARMCO 7348 CONCENTRATION ON ON BOND STRENGTH*

Set No.	Narmco 7343, Parts	Narmco 7348, Parts	Narmco 7139, Parts	Bell Peel Strength, piw					Lap Shear Strength, psi										
				RT				-320°F				RT				-320°F			
				Avg	High	Low	N	Avg	High	Low	N	Avg	High	Low	N	Avg	High	Low	N
311	100	0	12.5	113	114	111	5	77	79	76	4	3420	4500	2400	24	7980	8350	7450	8**
312	90	10	14.0	100	111	93	5	89	92	88	4	3850	4650	2950	24	8030	8300	7600	2+6**
313	50	50	19.8	78	84	68	5	50	62	40	4	5440	6060	4620	24	8200	8450	8000	8**
314	0	100	27.0	63	75	53	5	43	48	33	4	6970	7350	6300	16	8000	8450	7400	3+5**

N = number of specimens tested.

* = Adhesive contained 1.0 phr Dow-Corning Z-6040 siloxane and the adherends were primed with 0.2 pph hydrolyzed Z-6040 primer in methanol.

** = Metal Failure.

TABLE 53

EFFECT OF VARIOUS POLYURETHANE PREPOLYMER BLENDS ON BOND STRENGTH

Set No.	Prepolymer * Composition, Parts	7139 Curing Agent, Parts	NCO Content of Prepolymer, %	Shore D Hardness	Usable Pot Life	RT Lap Shear Strength, psi				-320°F Lap Shear Strength, psi	+200°F Lap Shear Strength, psi
						Avg	High	Low	N		
350	X-335, 100	8.5	2.8	--	3h 20m	2450	3020	1780	32	---	---
Misc	7343, 100	12.5	4.1	35	3h	3380	4840	2300	208	7475	1725**
355	X-333, 100	19.3	6.3	52	25m	5360	5700	4600	32	---	---
351	X-335, 50 X-334, 50	17.7	6.1	55	40m	4760	5180	4220	32	---	---
352	X-335, 50 7348, 50	17.7	6.1	58	29m	5090	5500	4160	32	---	---
346	7343, 50 X-334, 50	19.8	6.7	57	35m	4900	5640	2200	32	---	---
347	7343, 50 7348, 50	19.8	6.7	56	15m	5660	6000	5000	32	---	---
356	X-333, 50 X-334, 50	23.1	7.8	62	18m	5620	5990	5000	32	---	---
357	X-333, 50 7348, 50	23.1	7.8	63	17m	6050	6780	5480	32	---	---
Misc	X-334, 100	27.0	9.3	73	5m	6485	7490	4700	32	8300	2090
Misc	7348, 100	27.0	9.4	73	4m	6490	7350	4500	104	8030	2965

* Adhesive contains 1.0-phr Z-6040 based on total prepolymer weight.

** Adhesive contains no Z-6040 integral blend.

N = number of specimens tested.

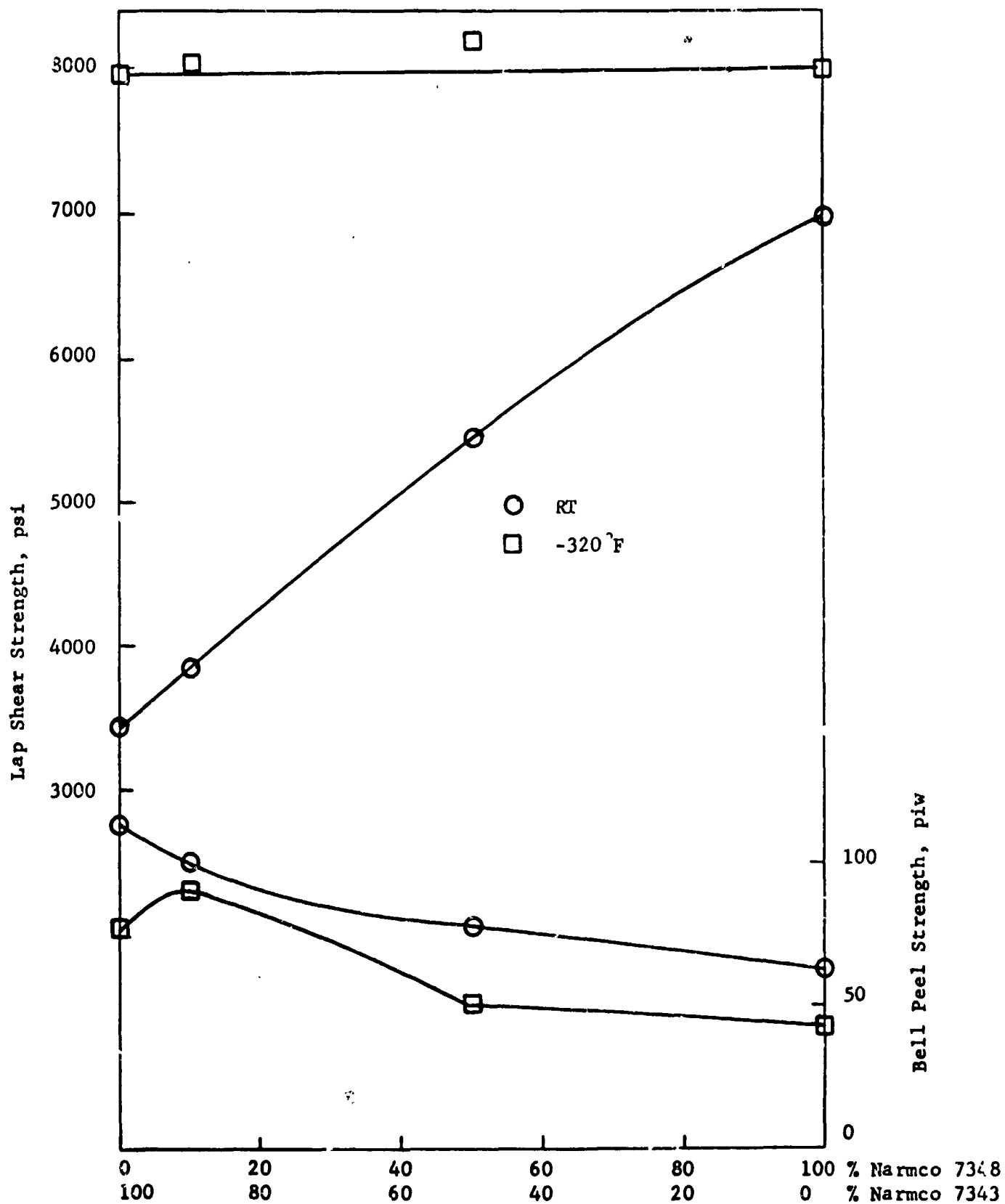


Figure 15. Effect of Narmco 7348 on Bond Strength

Figure 16 and 17 compare room temperature lap shear strength data with Shore D hardness and isocyanate (NCO) content of the prepolymer. The figures show that room temperature bond strength is improved with a high NCO content prepolymer which, in turn, results in a harder (less elastomeric) cured adhesive. Note in Figure 16 that test data obtained at -320°F falls on the same line as hardness/bond strength data obtained at room temperature.

Although the best bond strengths were obtained with Narmco 7348 and X-334 prepolymers, the usable pot life of these adhesives with Narmco 7139 is only 4 to 5 minutes. This short pot life makes the adhesive unusable for most applications. Figure 18 is a comparison of the usable pot life of the adhesive blends with room temperature lap shear strength. This information can be used to obtain an optimum bond strength for a required pot life, or vice versa.

During another study (shown in Table 54), Narmco 7348 bonds made either with or without Dow-Corning Z-6040 integral blend and hydrolyzed Z-6040 primer were compared. The data indicated that the primer and blend are needed to produce the bond strength shown above; nevertheless, excellent results were obtained even without the Z-6040 siloxane additives.

It had already been shown that Narmco 7343 adhesive is seriously affected by humidity. Theoretically, Narmco 7348 adhesive should be more adversely effected by humidity than the 7343 adhesive because of its higher isocyanate content; it was shown that water pickup is related to carbonyl (isocyanate) concentration.

To compare the effect of humidity on 7348 adhesive versus 7343 adhesive, bonds were made and then subjected to boiling water for 2 hours. As shown in Table 55, this accelerated test failed to produce any significant changes. This indicates that the loss of strength caused by humidity may be more dependent on time than on concentration. Also, the unexpected strength retention after the 2-hour water boil may have been the result of a "postcure" at 212°F.

Slow Amine Curing Agents

As discussed in the previous section, some excellent bond strengths were obtained with blends of Narmco 7343 and Narmco 7348 adhesives, cured with Narmco 7139 curing agent. While the 7348 and X334 adhesives give generally better bond strengths than any of the blends, their pot life at room temperature is limited to about 4 minutes. The short pot life of the 7348/7139 system is impractical for most applications; however, pot life can be increased through the use of slower amine curing agents and/or a blending of 7348 adhesive with longer pot life adhesives such as 7343 or X333.

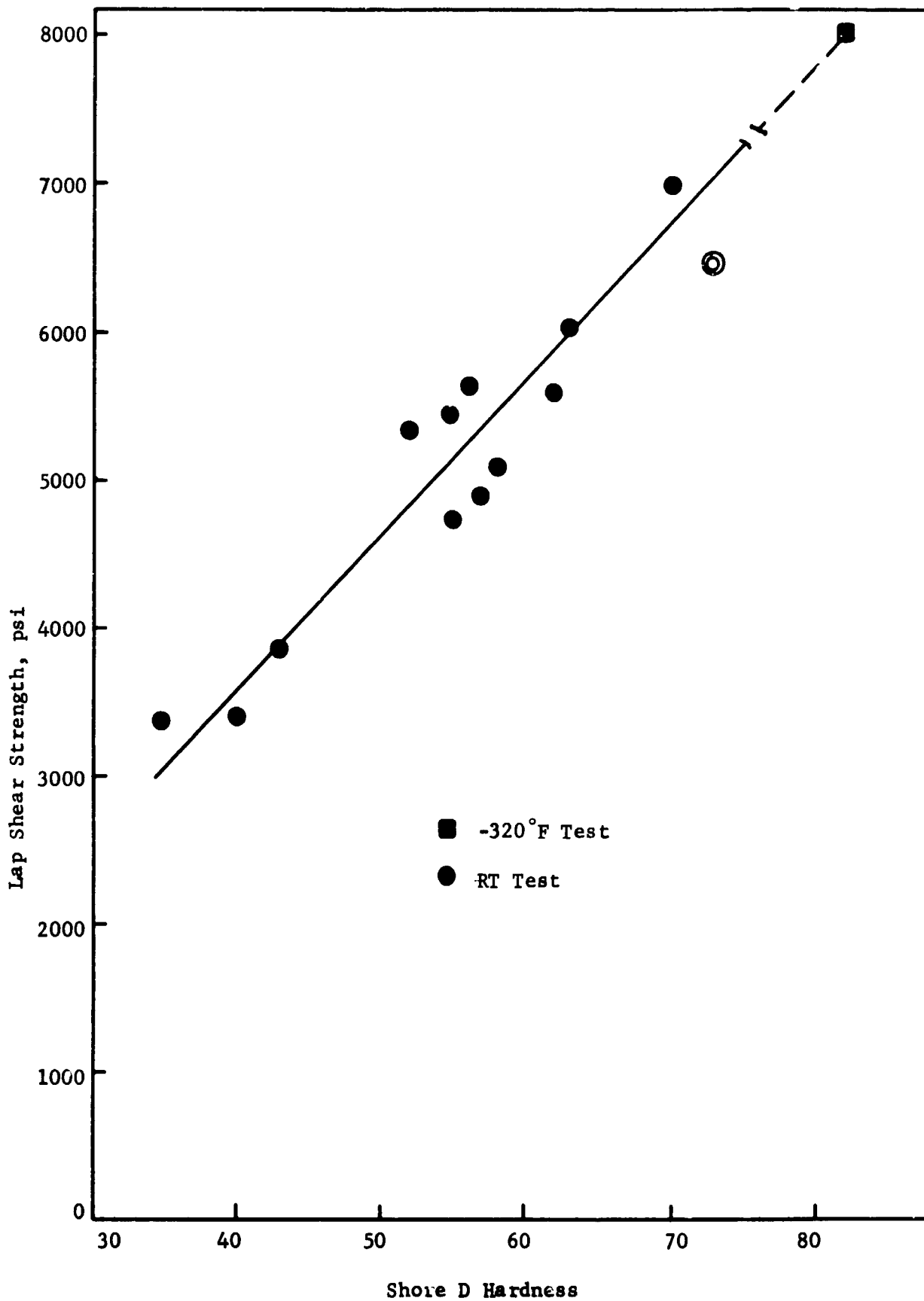


Figure 16. Comparison of Shore D Hardness and Lap Shear Strength for various Polyurethane Adhesive Blends

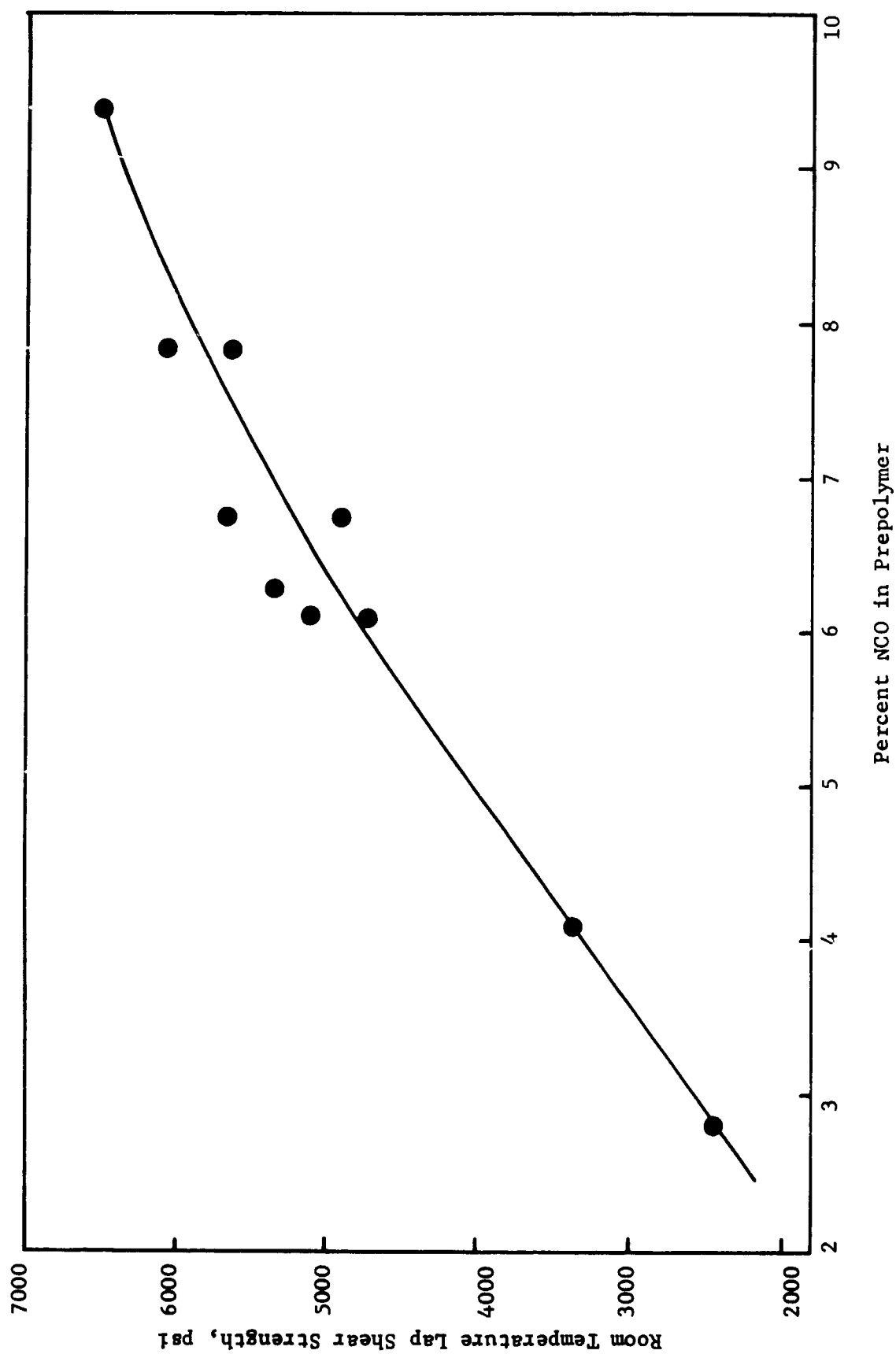


Figure 17. Effect of Prepolymer NCO Content on Room Temperature Lap Shear Strength for Various Polyurethane Adhesive Blends

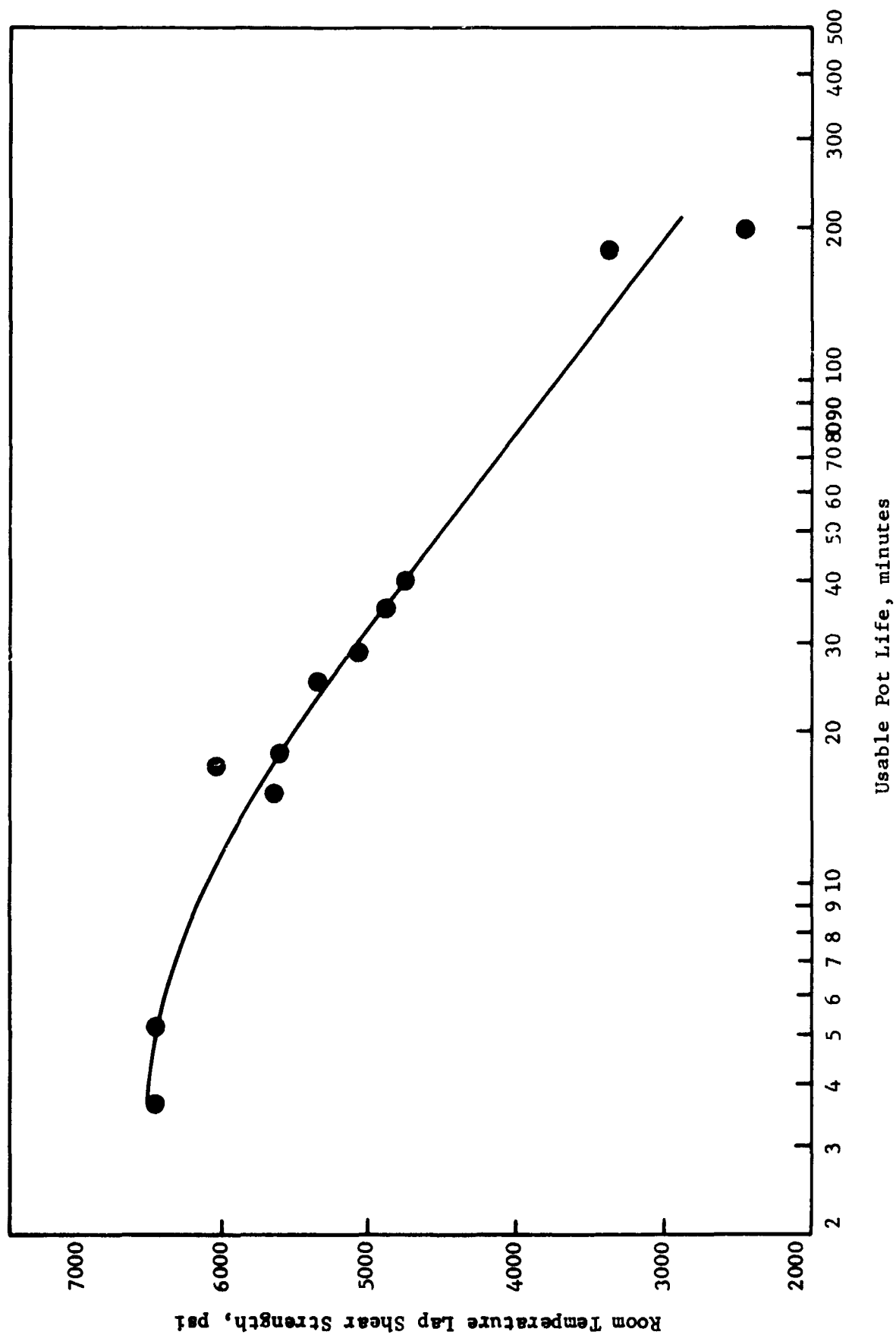


Figure 18. Comparison of Room Temperature Lap Shear Strength and Usable Pot Life for Various Polyurethane Adhesive Blends

TABLE 54

EFFECT OF Z-6040 PRIMER AND Z-6040 INTEGRAL LEND

Set No.	1.0-phr Z-6040 Integral Blend	0.2-phr Hydrolyzed Z-6040 Primer	Lap Shear Strength, psi					Bell Peel Strength, piw				
			-320					-320				
			Avg	High	Low	N		Avg	High	Low	N	
315	No	No	7350	8100	6400	8		5480	6000	4340	24	
Misc.	Yes	Yes	8030	9300	6100	49		6490	7350	4500	104	

N = number of specimens tested.

TABLE 55

EFFECT OF 2-HOUR WATER BOIL ON NARMCO 7343 AND 7348 ADHESIVE

Set No.	Adhesive	7139, phr	Test Temp., °F	Lap Shear Strength, psi					Bell Peel Strength, piw				
				Normal					Normal				
				Avg	High	Low	N		Avg	High	Low	N	
317	7343	12.5	RT	3110	3880	2340	24		3090	3730	2380	24	
317	7343	12.5	-320	6970	7760	6000	8		6460	7500	5020	8	
318	7348	27.0	RT	6450	6750	5850	24		6540	7000	6000	24	
318	7348	27.0	-320	8390	8840	7700	8		8180	8760	7300	8	

Notes:

N = number of specimens tested.

Adhesive contains 1.0-phr Z-6040 siloxane and adherends primed with 0.2-phr hydrolyzed Z-6040 primer.

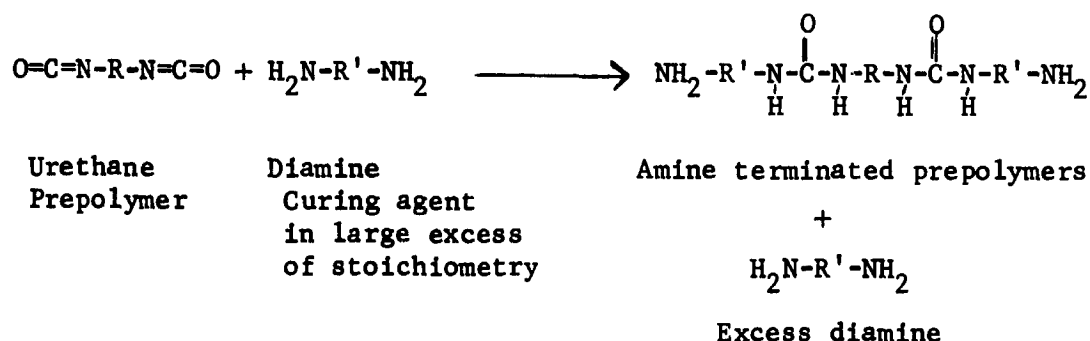
Two types of curing agents are slower than Narmco 7139; alcohols and hindered amines. In previous work using multifunctional alcohols, however, the cured adhesives produced very poor bond strengths.

Several hindered amine curing agents similar to Narmco 7139 were studied. Of these, only Narmco 7148 substantially increased the pot life of 7348 adhesive. When 7148 curing agent was used as a melted solid at 110°C, adhesive pot life was increased to 20 minutes (see Figure 19). Also, Narmco 7148 forms a super-cooled liquid (paste) at room temperature. When the paste is mixed with Narmco 7348 adhesive, pot life is increased to 40 minutes because of the lower mixing temperature involved.

The first bonds made from Narmco 7348 adhesive and Narmco 7148 curing agent were lower in strength than bonds made using Narmco 7139 curing agent (as shown in Table 56). Also, a series of bonds were made from blends of Narmco 7343 and 7343 adhesive using Narmco 7148 curing agent. The bond strengths obtained with the blended systems are shown in Table 57. The lower strengths obtained are attributed, at least in part, to the presence on moisture in the curing agent. After the bonds were made, it was found that the curing agent lost 1.8% by weight after drying. The water caused incorrect stoichiometry in the adhesive system and appreciable foaming. Another possible cause of the low bond strengths may have been that the cure cycle (16 hours at room temperature plus 24 hours at 160°F) was insufficient, inasmuch as Narmco 7148 curing agent is less reactive than Narmco 7139 curing agent.

Work was repeated using dry Narmco 7148 curing agent and a cure cycle of 4 days at 160°F. The data in Table 56 are compared with the previous bond strengths. The bond strengths obtained using the new conditions produced greater average tensile shear strengths, although the Bell peel strengths were not affected significantly.

Other systems were formulated from several urethane prepolymers which had been mixed with a very large excess of Narmco 7148 curing agent. When large stoichiometric excess of Narmco 7148 amine is added to the urethane prepolymer, the following reaction occurs.



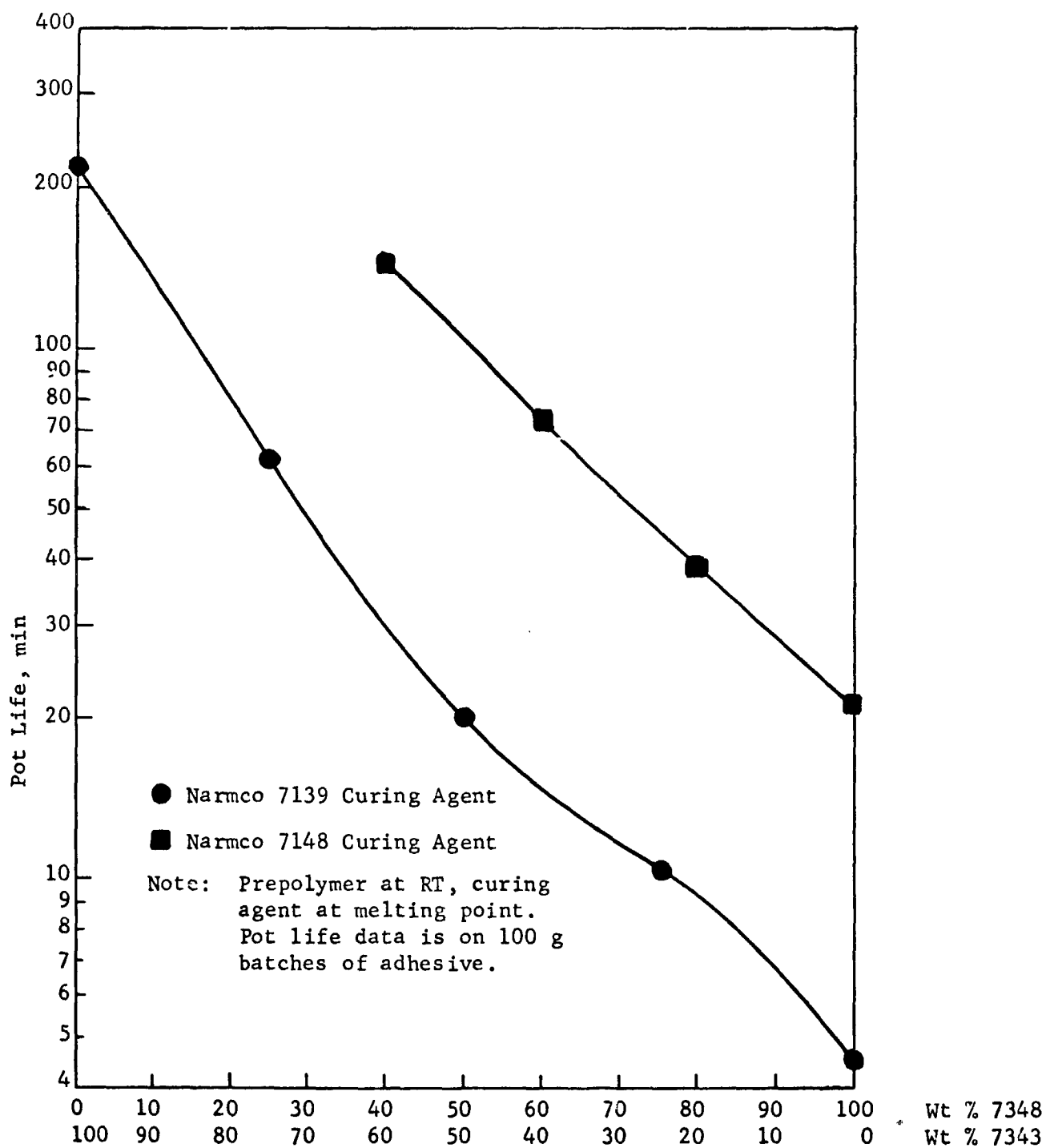


Figure 19. Pot Life of 7343/7348 Blends with 7139 and Dry 7148 Curing Agents

TABLE 56

COMPARISON BETWEEN NARMCO 7139 AND 7148 CURING AGENTS
WITH NARMCO 7348 ADHESIVE*

Cure Cycle	Curing Agent Conditions	Test Temp, of	Set No.	Lap Shear Strength, psi			Bell Peel Strength, piw				
				Avg	High	Low	N	Avg	High	Low	N
Narmco 7139 Curing Agent											
27.0-phr 7139, 4 days @ 160°F	as received	-320 RT +200	339	8350	9100	7700	12	--	--	--	
				6410	6700	5900	24	67	87	59	8
				3500	3940	2710	12	175	198	156	5
27.0-phr 7139, 1 day @ 160°F	as received	-320 RT +200	319	6910	8000	6100	12	18	23	13	
				6480	6900	5700	24	81	112	63	8
				2590	3090	1930	12	199	218	183	5
Narmco 71'8 Curing Agent											
30.4-phr 7148, 4 days @ 160°F	dried	-320 RT +200	340	7330	8300	6500	12	--	--	--	
				6110	6500	5250	24	64	82	49	8
				2790	3350	2010	12	116	125	109	5
30.4-phr 7148, 1 day @ 160°F	as received (determined not dry)	-320 RT +200	320	3530	4680	2200	10	5	6	5	
				3700	4680	2520	22	58	80	36	8
				750	1040	510	10	45	53	39	5

* Adhesive contains 1.0-phr Z-6040 siloxane, and adherends are primed with 0.2-phr hydrolyzed Z-6040 primer.

N = number of specimens tested.

TABLE 57

BLEND OF NARMCO 7343 AND 7343* CURED WITH NARMCO 7148 ADHESIVE**

Set No.	7343, Parts,	7348, Parts	7148, Parts	Lap Shear Strength, psi					Bell Peel Strength, piw									
				-320°F					-320°F									
				Avg	High	Low	N	Avg	High	Low	N	Avg	High	Low	N			
321	0	100	30.4	4025	4950	2850	10	4390	5000	3450	23	7	6	6	123	149	103	9
322	20	80	27.1	5910	7450	4400	10	4280	4900	3680	23	17	16	6	103	112	95	9
323	40	60	24.0	5930	7400	5100	9	3330	4600	850	23	20	16	6	85	97	73	9

* Adhesive contains 1.0-phr Z-6040 siloxane. Adherends primed with 0.2-pph hydrolyzed Z-6040 primer.

** 7148 curing agent used as received and determined not dry.

N = number of specimens tested.

The resulting material is an amine-terminated prepolymer with remaining excess diamine curing agent. The mixture cannot cure itself into a solid because of the large stoichiometric excess of amine which immediately terminates any chain formation. The resulting amine mixture can then be used as a curing agent for Narmco 7348 adhesive as well as other urethane prepolymers.

Taffylike semisolid mixtures and solids resulted when several urethane prepolymers were treated in the above manner. The solid mixtures had to be melted before they could be used with Narmco 7348 adhesive, and the temperature increase resulted in pot lives near that of the melted Narmco 7148 curing agent. Pot life increased substantially when the semi-solids were used with Narmco 7348 adhesive because of the lower mixing temperature and the decrease in the relative concentrations of the reactive group. The high viscosity of these mixtures complicated attempts to blend them with the adhesive and therefore, makes them impractical for production bonding. Table 58 lists the information, physical properties, and the usable pot life of Narmco 7348 adhesive for five of the systems discussed.

TABLE 58
COMPARISON OF CURING AGENTS

Curing Agent Formulation, % by Weight	Physical Properties When Mixed with 7348 Adhesive	Usable Pot Life* with Narmco 7348 Adhesive
Narmco 7139 100%	Liquid @ 110°C	4 min
Narmco 7148 100%	Liquid @ 110°C	20 min
Narmco 7148 100%	RT super-cooled liquid	40 min
Narmco 7148 70% Narmco 7343 30%	Taffylike semisolid	2 hr
Narmco 7148 50% Narmco 7343 50%	Taffylike semisolid	2 hr
Narmco 7148 70% Narmco X-333 30%	Taffylike semisolid	2 hr, 40 min

* Length of time a 100-g mass remains spreadable after addition of curing agents.

EXPERIMENTAL

Table 59 compares bonding procedures used during the course of the research. This table is keyed to detailed process steps listed below, and is also keyed to photographs showing individual process steps.

The adherends were 2024-T3 clad aluminum and the bonded specimens conformed in size to dimensions given in Appendixes D* and E.**

The specimens were identified by a set number which represented a single batch of catalyzed adhesive, a letter representing specimen cut from the panel.***

Mechanical testing was accomplished in an Instron or Tinius-Olsen testing machine in accordance with Appendixes D and E. Testing at -320°F was conducted in boiling liquid nitrogen. Elevated temperature testing at 200°F was accomplished in a circulating air oven with temperatures monitored by thermocouples.

DETAILED PROCESS STEPS

1. Remove burrs on edge of panels with file.
2. Remove mill lettering with methyl ethyl ketone (MEK) or trichloroethylene (TCE) wipe.
3. Degrease, using 10-minute vapor degrease at 194° - 212°F .
4. Etch panels 10.0 minutes at 151° - 160°F . Allow panels to drain 10 to 20 seconds. Etch solution compositions: distilled water, 30 pbw; sulfuric acid, 10 pbw; sodium dichromate dihydrate, 4 pbw. Control limits: H_2SO_4 34 to 42 oz/gal; $\text{Na}_2\text{Cr}_2\text{O}_7$, 11 to 14 oz/gal.
5. Spray-rinse thoroughly with cold tapwater followed by two rinses with running cold distilled water.
6. Oven-dry for 10 minutes at 140° - 150°F .
7. Mask all areas not to be bonded using cellophane tape and masking tape.
8. Spray a solution of 0.2-pph Dow-Corning Z-6020 primer in absolute, denatured ethanol onto adherends, using compressed gas spray pack. Allow primer to dry 2 hours at room temperature.

* Figures 46 and 47.

** Figure 51.

*** Figures 44 and 45.

9. Spray a solution of 0.2-pph Dow-Corning Z-6040 primer in absolute, de-natured ethanol onto adherends, using compressed gas spray pack. Allow primer to dry 2 hours at room temperature.
10. Spray a solution of Z-6040 hydrolyzed siloxane primer onto the adherends. Prepare the primer by mixing 1.0 g of Dow-Corning Z-6040 siloxane with 10.0 g of 1.0% acetic acid and shake for 10 minutes. Add 2.2 g of this mixture to 100 g of methanol and spray the adherends 2 hours prior to bonding.
11. Cover panels with clean dry paper until ready for bonding. Bond panels within 6 hours of etching.
12. Weigh adhesive and curing agent into separate metal containers that have been degreased with TCE and dried 15 minutes at 150°-160°F.
13. Heat the curing agent and adhesive in the same vacuum oven for 40 minutes at 210°F with a final pressure of 1 to 3 mm Hg. Cool the adhesive to 160°F. Pour the molten curing agent into the adhesive and mix 1 minute by hand followed by 4 minutes in a Hobart Model N 50 eccentric rotary mixer. Mixing ratio 12.5 parts Narmco 7139 curing agent to 100 parts Narmco 7343 adhesive.
14. Heat the curing agent and adhesive in the same vacuum oven for 40 minutes at 210°F with a final pressure of 1 to 3 mm Hg. Cool the adhesive to 160°F. Add 1 phr of Z-6040 siloxane and mix 1 minute by hand followed by 4 minutes in a Hobart Model N 50 eccentric rotary mixer. Mixing ratio 12.5 parts Narmco 7139 curing agent to 100 parts Narmco 7343 adhesive.
15. Add 1 phr Z-6040 siloxane to ambient temperature Narmco 7348 adhesive and mix 1 minute by hand. Melt Narmco 7139 curing agent, pour into 7348 adhesive, and mix 1.0 minute by hand. Mixing ratio is 27 parts Narmco 7139 curing agent to 100 parts 7348 adhesive.
16. Mix 27 phr of molten Narmco 7139 curing agent with ambient temperature Narmco 7348 adhesive. Mix 1.0 minutes by hand.
17. Apply warm adhesive to both surfaces of ambient temperature adherends.
18. Sprinkle glass beads on bondline using salt shaker technique. Bell peels contain 9.7-mil (60-80 mesh) glass beads while lap shear joints contain 4.1-mil (140-200 mesh) beads.
19. Unite panels and stack on curing fixtures, using doublers, spacers, and fluorocarbon film separator, where necessary. Bell peel panels are stacked to a maximum height of 6 panels, while lap shear panels are stacked to a maximum height of 4 panels.
20. Close Bell peel panels in a room temperature press at 25 psi.

21. Vacuum-bag, using envelope bagging technique. Cure overnight (for 16 hours) at a vacuum of 10-15 in. Hg. Remove from vacuum bag and remove separators, spacers, and masking tape. Number panels for identification.
22. Postcure at $24 \pm 1/2$ hour at 160°F.
23. Store specimen panels in desiccator bags with Drierite desiccant prior to specimen cutting.
24. Cut three 1-in. wide Bell peel specimens from center of 4-in. wide Bell peel panel. Cut eight lap shear specimens from lap shear panels.
25. Store specimens in desiccator bags up to time of testing.
26. Test specimens the calendar week following manufacture, except as noted.

TABLE 59
BONDING PROCEDURES

Bonding Procedure →			8	9	10	11	12	13	14	15	16
Figure No.	Operation	Key No.									
20	Deburr	1	X	X	X	X	X	X	X	X	X
21	Solvent wipe	2	X	X	X	X	X	X	X	X	X
22	Vapor degrease	3	X	X	X	X	X	X	X	X	X
23	Etch	4	X	X	X	X	X	X	X	X	X
24	Rinse	5	X	X	X	X	X	X	X	X	X
25	Dry	6	X	X	X	X	X	X	X	X	X
26, 27	Mask	7	X	X	X	X	X	X	X	X	X
28	Z-6020 prime	8		X		X					
	Z-6040 prime	9					X				
	Hydrolyzed prime	10						X	X	X	
	Protect panels	11	X	X	X	X	X	X	X	X	X
	Weigh out adhesive	12	X	X	X	X	X	X	X	X	X
29, 30, 31	Mix adhesive	13	X	X	X	X	X	X			
	↓	14							X		
		15								X	
		16									X
32, 33, 34, 35	Apply adhesive	17	X	X	X	X	X	X	X	X	X
36	Bondline control	18	X	X	X	X	X	X	X	X	X
37, 38, 39, 40	Unite panels	19	X	X	X	X	X	X	X	X	X

Continued on next page

TABLE 59 (Continued)

Bonding Procedure →			8	9	10	11	12	13	14	15	16
Figure No.	Operation	Key No.									
41 44, 45	Close panels	20	X	X	X	X	X	X	X		
	Cure	21	X	X	X	X	X	X	X	X	X
	Post Cure	22	X	X	X	X	X	X	X	X	X
	Dry storage	23	X	X							
	Cut specimens	24	X	X	X	X	X	X	X	X	X
	Dry storage	25	X	X							
	Test	26	X	X	X	X	X	X	X	X	X

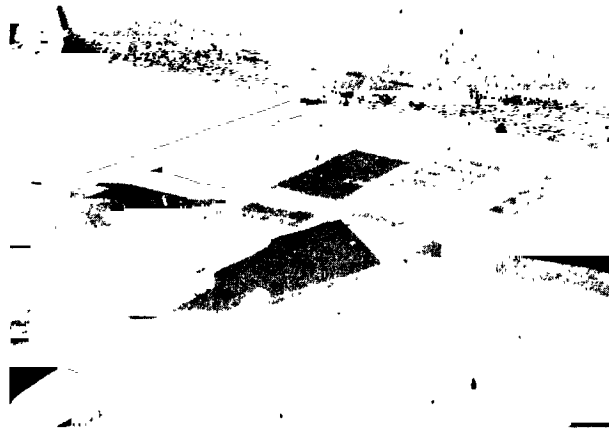


Figure 20. Deburring of Bell Peel and Lap Shear Panel Adherends

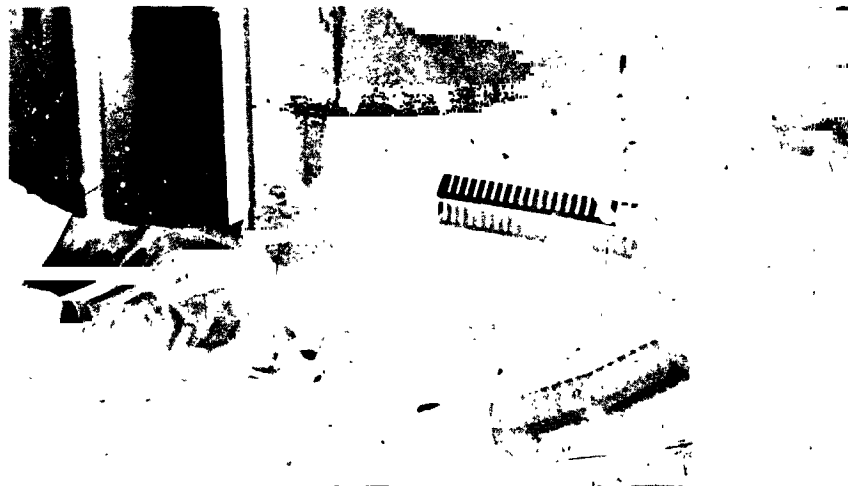


Figure 21. Removal of Mill Lettering with Methyl Ethyl Ketone (MEK)

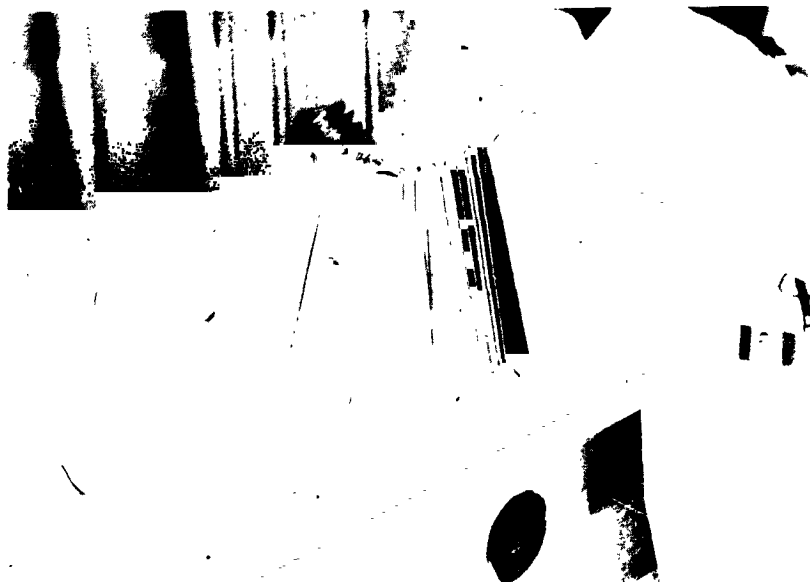


Figure 22. Vapor Degreasing of Bell Peel Panel Adherends with Trichloroethylene



Figure 23. Etching of Bell Peel Panel Adherends with Sulfuric Acid/Sodium Dichromate/Water Solution



Figure 24. Distilled Water Rinse
after Etching

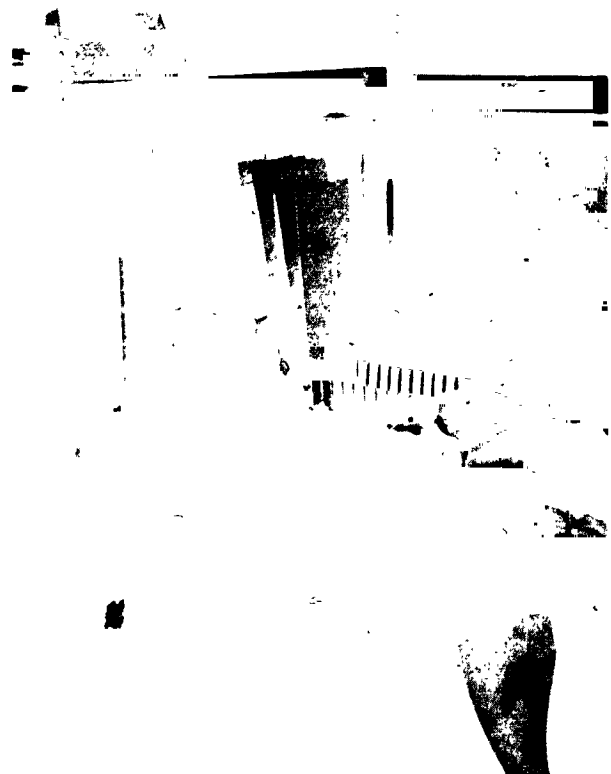


Figure 25. Oven Drying of Bell Peel
Panel Adherends at 140°-
150°F



Figure 26. Tape Masking of Nonfaying Surface of Bell Peel Panel Adherend



Figure 27. Tape Masking at Faying Side in the Peel Initiation Area (To start peel and allow installation in test fixture)

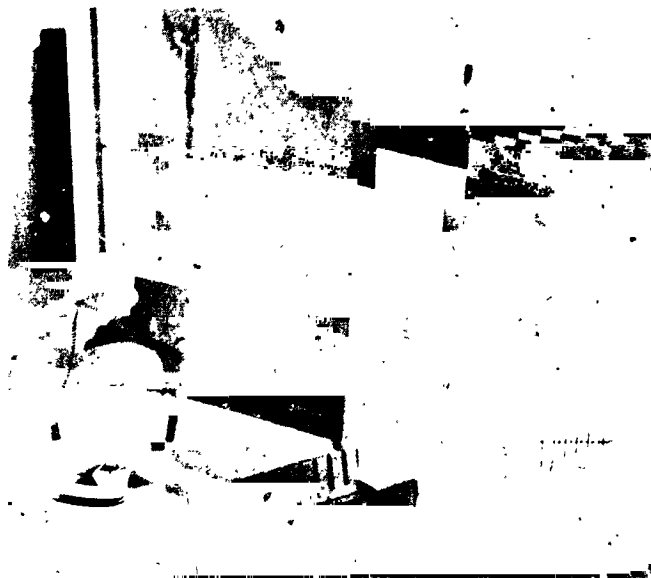


Figure 28. Spray Application of
Siloxane Primer to Bell
Peel Panel Adherend



Figure 29. Placing of Narmco 7343
Prepolymer and Narmco
7139 Curing Agent in
Vacuum Oven

Figure 30. Heating and Degassing of
Narmco 7343 Prepolymer
and Narmco 7139 Curing
Agent in Vacuum Oven

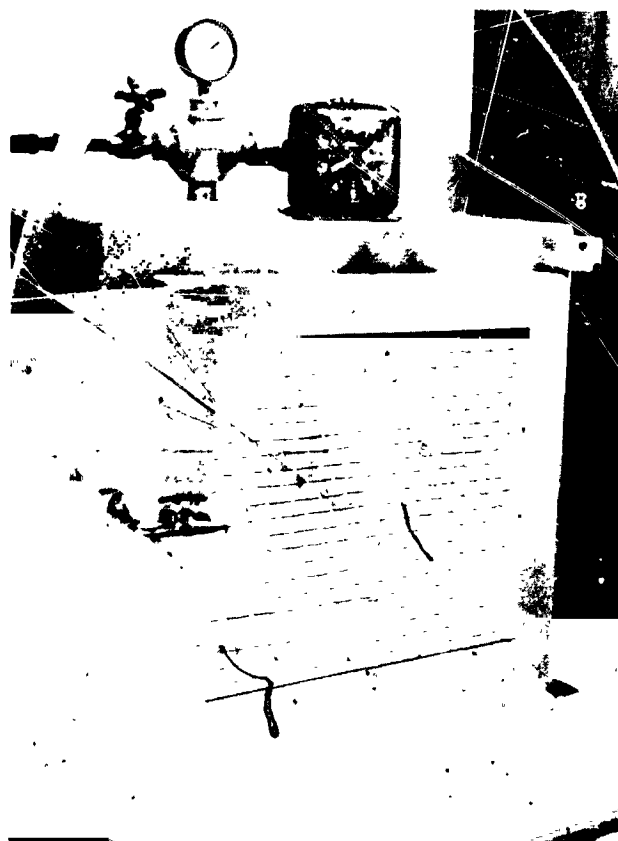


Figure 31. Mixing of Adhesive and
Curing Agent in a Ho-
bart Eccentric Rotary
Mixer

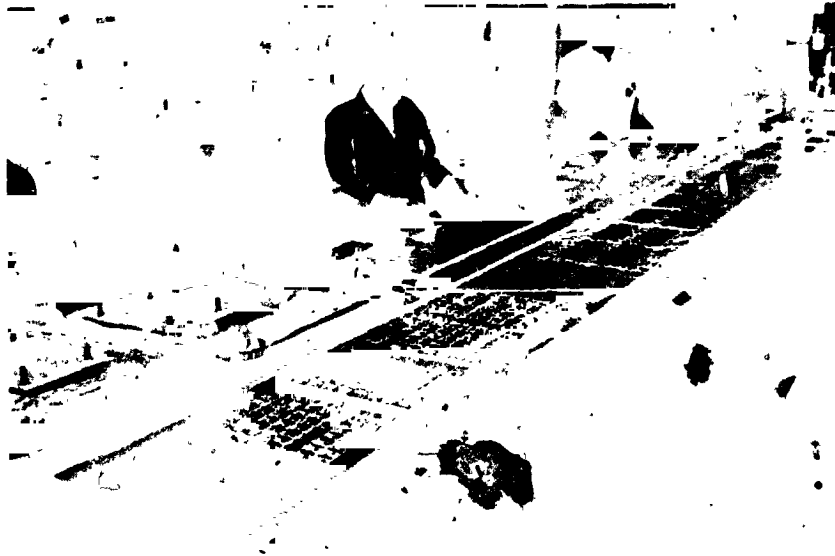


Figure 32. Bell Peel and Lap Shear Panel Adherends Preparatory to Daily Layup Operation

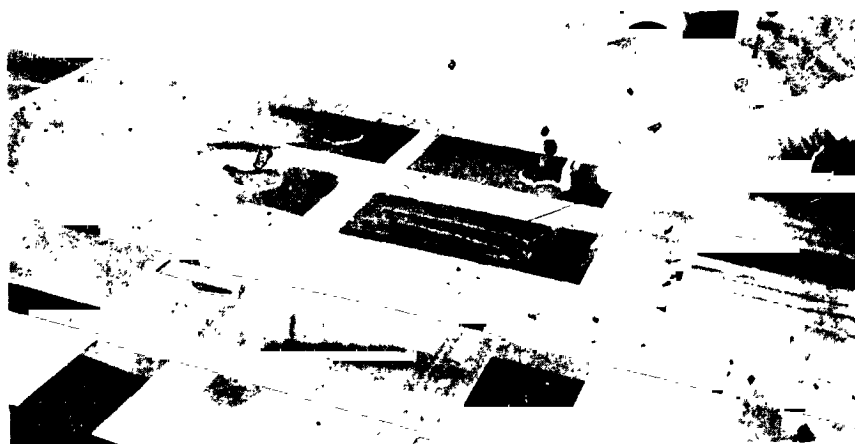


Figure 33. Application and Spreading of Adhesive to Faying Surfaces of Bell Peel Panel Adherends



Figure 34. Application and Spreading of Adhesive to Faying Surfaces of Lap Shear Panel Doubler

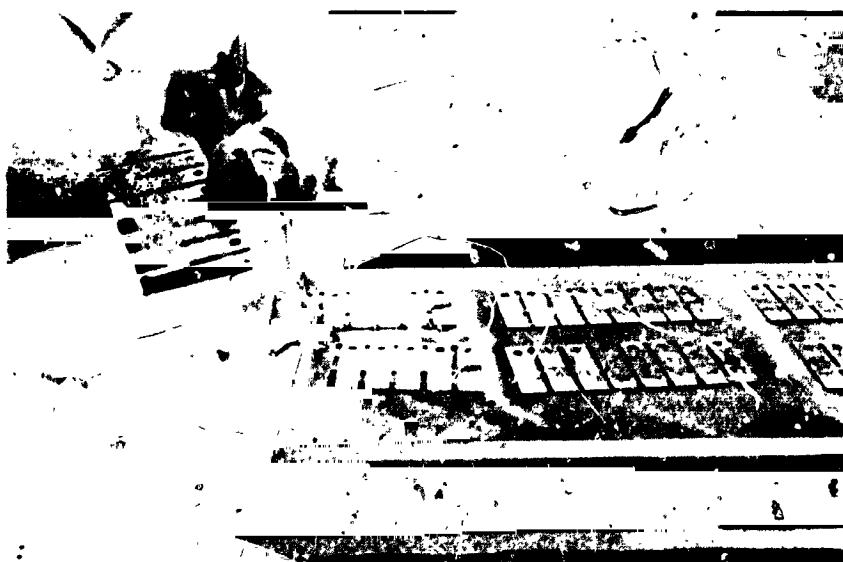


Figure 35. Application of Adhesive to Faying Overlap Area of Lap Shear Panel Adherend



Figure 36. Applying Glass Beads to Spread Adhesive for Bondline Thickness Control



Figure 37. Uniting the Bell Peel Panel Components after the Adhesive has been Applied

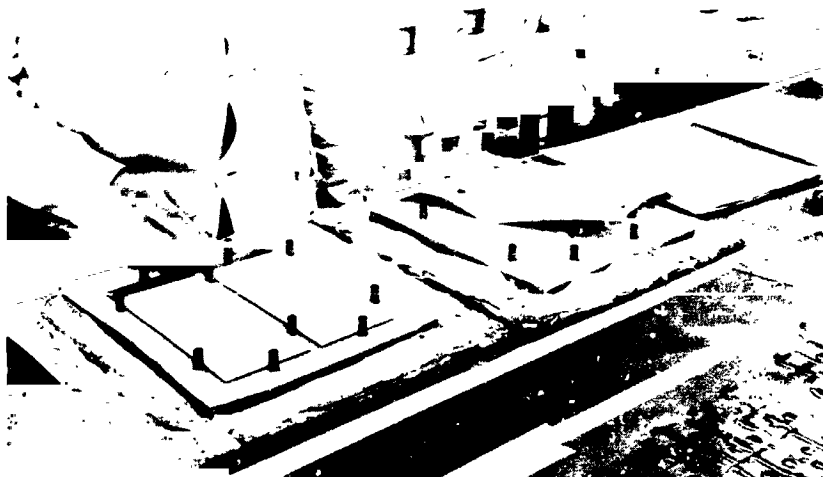


Figure 38. Stacking Assembled Bell Peel Panels
on the Curing Fixture

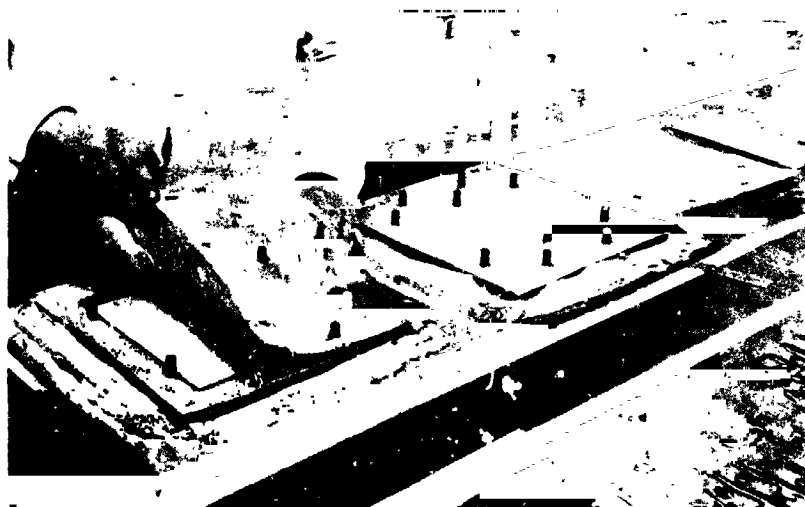


Figure 39. Interposing Fluorocarbon Fabric as
Separator Films Between Panels

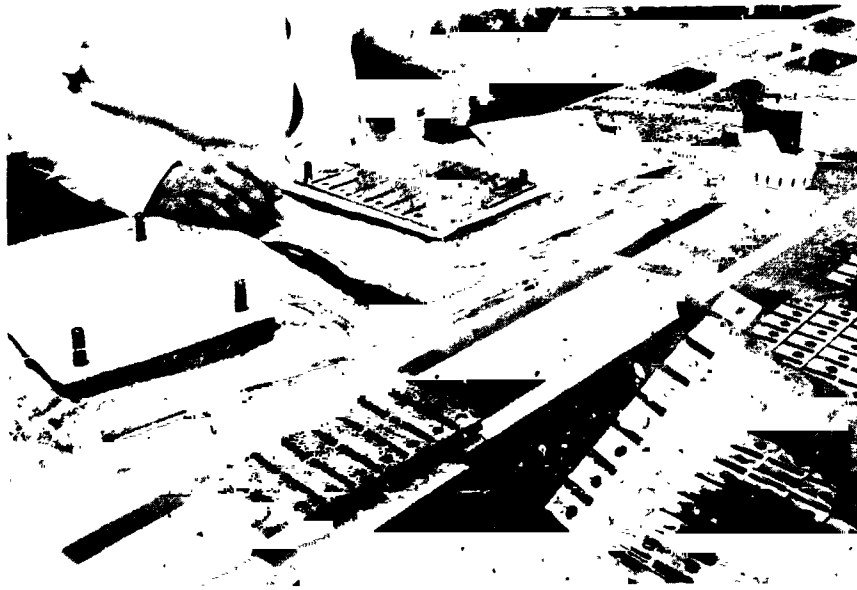


Figure 40. Stacking Lap Shear Panels and Doubler Panels on the Curing Fixture



Figure 41. Stacked Bell Peel Panels on Curing Fixture being Pressed at Room Temperature and 25 psi to Close Adherends to Glass Beads



Figure 42. Inserting Curing Fixture with Assembled Panels into Envelope Vacuum Bag



Figure 43. Bell Peel and Lap Shear Panels undergoing Overnight (16-19 hours) Room Temperature Cure at 10-15 in. Hg Vacuum Pressure



Figure 44. Lap Shear Test Specimen

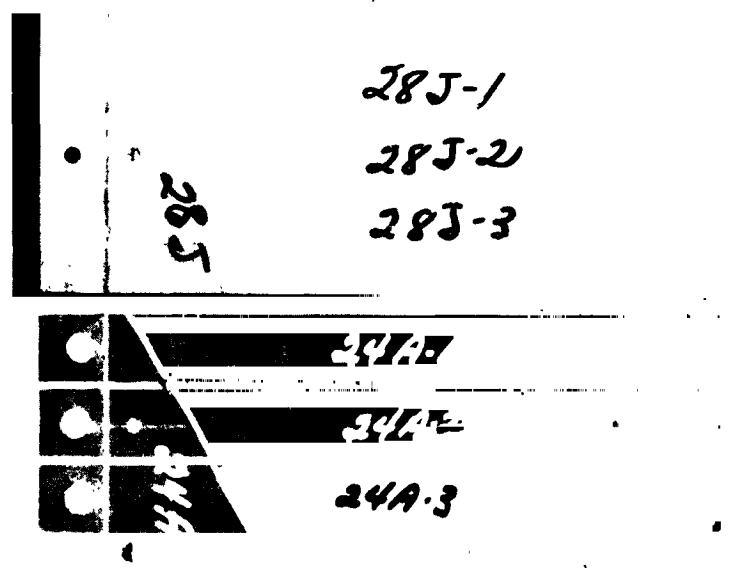


Figure 45. Bell Peel Panel with Three Bell Peel Test Specimens

CONCLUSIONS

1. Dow-Corning Z-6040 and Z-6020 siloxanes used as adherend primers increase bond strength and improve humid storage strength retention. Also, Z-6040 siloxane hydrolyzed with acetic acid and used as a primer in conjunction with 1-phr Z-6040 blended in Narmco 7343 adhesive gives excellent bond strength performance in both 100% humid conditions and ambient humidity conditions.
2. Variations in bonding processes have little significant improvement on bond strengths, except for slight improvements when the adhesive is mixed in a hand emulsifier and a small improvement in -320°F bond strengths when the adhesive is not degassed.
3. No significant improvement in overall bond strengths results from modification of the standard Narmco 7343/7139 adhesive system.
4. Blending Narmco 7343 adhesive with urethane adhesive with high NCO content results in a steady improvement in room temperature and elevated temperature strengths as adhesive hardness and NCO contents increase.
5. Narmco 7148 amine curing agent increases the pot life of urethane adhesive five times longer than Narmco 7139 curing agent. Narmco 7148 as a super-cooled room temperature liquid results in a tenfold increase in pot life over Narmco 7139 curing agent.

RECOMMENDED FUTURE WORK

Formulation changes to Narmco 7343 adhesive should be examined, with the objectives of increasing hardness and reducing elasticity. This is recommended because it has already been demonstrated that similar but harder polyurethane resins produce significantly increased overall bond strength.

Concurrently with the above, a slow amine (preferably liquid at room temperature) curing agent system should be formulated for use with the above adhesive. A slow curing agent will be required because the harder, higher isocyanate content polyurethanes inherently cure too rapidly when standard Narmco 7139 curing agent is used.

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1. S. Sterman and J. S. Marsden, "Silane Coupling Agents as Integral Blends in Resin-Filler Systems," Modern Plastics, July 1963, pp. 125-177
2. "Dow Corning Z-6040 Silane," Dow Corning Bulletin 03-012, July 1964
3. S. Sterman and J. B. Toogood, "How to Promote Adhesion with Silicones and Silanes," Adhesive Age, July 1965
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5. S. L. Reegan, Journal of Applied Polymer Science, 10, 1247-1259 (1966)

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APPENDIX A

AVERAGE STRENGTHS OF BONDS MADE WITH VARIOUS PROCEDURES

Table 60 compares test results of all bonds made by various procedures.

APPENDIX A

TABLE 60

AVERAGE STRENGTHS OF BONDS MADE BY VARIOUS PROCEDURES

Notes	Primer	Storage ~ 8 Days		Bell Peel			Lap Shear		
				-320°F	RT	+200°F	-320°F	RT	+200°F
Procedure 8	None	Dry	Avg	63	57	31	8090	2210	439
			High	81	104	40	9470	3200	544
			Low	32	34	23	5800	1190	256
			N	325	412	16	416	535	32
Procedure 10	None	Ambient	Avg	34	44	20	7110	1693	323
			High	49	67	29	8860	2780	452
			Low	17	25	13	4250	720	206
			N	25	153	16	64	416	32
Procedure 9	Z-6020	Dry	Avg	89	142		8748	3760	
			High	109	231	--	9630	5200	--
			Low	70	84		7260	2240	
			N	249	294		239	290	
Procedure 11	Z-6020	Ambient	Avg		131			2512	
			High	--	150	--	--	3820	--
			Low		120			1820	
			N		36			64	
-----	Z-6040	Dry	Avg	76	98		8450	2570	
			High	89	118	--	9210	3240	--
			Low	46	72		7770	1720	
			N	33	33		29	28	
Procedure 12	Z-6040	Ambient	Avg		78			2589	
			High	--	107	--	--	3780	--
			Low		29			1520	
			N		27			80	
Procedure 13	Z-6040 Hydro.	Ambient	Avg	73	68	68.5	8426	3122	1725
			High	89	134	94	9200	4750	3000
			Low	56	34	40	5300	1460	625
			N	18	81	18	64	448	64
1 phr Z-6040 Integral Blend	None	Ambient	Avg	73	128	92	8750	2667	1650
			High	87	176	112	9490	3990	2230
			Low	55	100	68	7950	1290	1090
			N	9	27	9	32	96	31

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TABLE 60 (Continued)

Notes	Primer	Storage ≈ 8 days		Bail Peel			Lap Shear		
				-320°F	RT	+200°F	-320°F	RT	+200°F
Procedure 14 1 phr Z-6040 integral blend	Z-6040 hydro.	Ambient	Avg	67	118	--	7475	3380	--
			High	75	152	--	--	4840	--
			Low	44	98	--	6300	2300	--
			N	8	46	--	16	208	--
1 phr Z-6040 20 phr Al filler inte- gral blend	None	Ambient	Avg	--	99	--	--	3100	--
			High	--	105	--	--	3500	--
			Low	--	93	--	--	2200	--
			N	--	9	--	--	32	--
Procedure 15 100% Narmco 7348 1 phr Z-6040 integral blend 7139 curing agent	Z-6040 hydro.	Ambient	Avg	29	77	187	8030	6490	2965
			High	48	130	218	9300	7350	3940
			Low	13	53	156	6100	4500	1930
			N	13	35	10	49	104	31
100% Narmco 7348 1 phr Z-6040 integral blend 7148 curing agent	Z-6040 hydro.	Ambient	Avg	--	67	175	7330	6110	2790
			High	--	87	198	8300	6500	3350
			Low	--	59	156	6500	5250	2100
			N	--	8	5	12	24	12

N = number of specimens tested.

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APPENDIX B

RECOMMENDED BONDING PROCEDURE FOR NARMCO 7343 CRYOGENIC ADHESIVE

APPENDIX B

RECOMMENDED BONDING PROCEDURE FOR NARMCO 7343 CRYOGENIC ADHESIVE

1. Materials

- 1.1 Narmco 7343 adhesive^{*}
- 1.2 Narmco 7139 curing agent^{*}
- 1.3 Z-6020 silane^{**}
- 1.4 Z-6040 silane^{**}
- 1.5 Glacial acetic acid
- 1.6 Glass beads
- 1.7 Masking tape
- 1.8 Methyl ethyl ketone
- 1.9 Trichloroethylene
- 1.10 Methanol
- 1.11 Distilled water
- 1.12 Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$)
- 1.13 Sulfuric acid 98%

2. Adherend Preparation

- 2.1 Degrease adherends with suitable solvent such as methyl ethyl ketone or trichloroethylene. Vapor degreasing in trichloroethylene being the preferred method.
- 2.2 Etch panels using sodium dichromate/sulfuric acid etch solution (Notes 1, 2, and 3).
- 2.3 Spray rinse the adherends thoroughly with RT water, the final rinse to be RT distilled water (Note 4).
- 2.4 Dry adherends for 10 minutes at 140°-150°F (Notes 5 and 6).

* Narmco Materials Division of Whittaker Corporation, Costa Mesa, California

** Dow-Corning, Midland, Michigan

- 2.5 Prime adherend with hydrolyzed Z-6040 primer using any suitable application technique (Notes 7, 8, and 9).

2.5.1 Primer formulation Z-6040	1 part	} Shake ten minutes
1% acetic acid solution	10 parts	
methanol	500 parts	

- 2.6 After primer is dry to touch, rinse adherends with distilled water to remove acetic acid.
- 2.7 Mask areas which must remain free of adhesive with masking tape.
- 2.8 Protect adherends from contaminations prior to bonding.

3. Adhesive Mixing Procedure

- 3.1 Weigh adhesive and curing agent components into separate clean, dry metal containers. Mixing ratio shall be 11.0 \pm 0.5 parts Narmco 7139 per 100 parts Narmco 7343. Add additional 7139 curing agent to allow for curing agent which remains in container when components are mixed. Do not fill adhesive component container more than one-third full to allow for vacuum degassing step below.

- 3.2 Place both components in a preheated vacuum oven (Note 10) at 230°F under full vacuum. Allow the components to remain in vacuum oven until the bulk of the adhesive foam has broken and the curing agent has melted (about 20 minutes).

CAUTION: Adhesive container must be watched closely during initial part of degassing procedure to prevent frothing over.

- 3.3 Remove the adhesive component from the oven and mix in 1.0 parts of Z-6040 silane per 100 parts of adhesive.
- 3.4 Add the melted Narmco 7139 curing agent component to the 7343/Z-6040 blend. Begin mixing immediately to prevent crystallization of curing agent. Continue mixing until the adhesive is free of streaks, using proper mixing technique, and avoiding entrapping excess air (Note 11).

4. Bonding Procedure

- 4.1 Apply adhesive to both bonding surfaces.
- 4.2 Sprinkle glass beads onto adhesive for bondline thickness control. Bondline thickness shall be as specified by Engineering Design (Note 12).

- 4.3 Unite bonding surfaces, using holding devices as necessary to insure proper alignment and pressure (Note 13).
- 4.4 Cure at ambient temperature until adhesive has gelled (12-24 hours) (Note 14).
- 4.5 Remove bonding fixtures and masking tape.
- 4.6 Postcure 24 hours at 160°F or 12 days at 72°F.

5. Quality Control

- 5.1 Isocyanate content in 7343 prepolymer shall be 4.08 to 4.30% and the Brookfield viscosity shall be 20,000 to 30,000 cps.
- 5.2 Amine purity by HClO_4 method of the Narmco 7139 curing agent shall be in excess of 98.0%.
- 5.3 A coating representative of each production batch of adhesive and receiving the same cure and postcure of the production parts represented shall have an average Shore A hardness of 86-94.
- 5.4 The average of five lap shear specimens made from the same adhesive and receiving the same cure as the production parts represented shall have a bond strength of 2840 psi when tested at room temperature. The minimum bond strength for an individual specimen shall be in excess of 2165 psi (Note 15).

NOTES:

- (1) The following etch solution control limits have proven to be satisfactory. However, no work has been done to show that the solution is optimum for the Narmco 7343/7139 adhesive system.

11 to 14 oz/gal $\text{Na}_2\text{Cr}_2\text{O}_7$

34 to 42 oz/gal H_2SO_4

10 min @ 151°-160°F

- (2) Work with paste etches have shown them to be satisfactory, however the specific paste etch should be evaluated prior to use.

- (3) Use of an alkaline cleaner prior to etching may prove useful for unusually contaminated adherends. However, this treatment is not beneficial for normally clean aluminum.

Alkaline cleaner composition 3 oz/gal Na_3PO_4

3 oz/gal Na_2CO_3

1 to 3 minutes at 140° to 158°F

- (4) The use of hot rinse water must be avoided.
- (5) The use of higher temperatures must be avoided. However, longer ambient temperature during periods have proven to be satisfactory.
- (6) Studies have shown that etched adherends may be stored for periods up to 1 month at ambient conditions provided they are protected from contamination.
- (7) Primer drying times between 1/2 hour and 24 hours have proven to be satisfactory.
- (8) This primer is stable for only a few minutes and must be applied immediately.
- (9) The priming procedure can be simplified somewhat by using a solution of 1 part Z-6040 or Z-6020 in 500 parts methanol and omitting step 2.6. These primers produce almost equivalent results to the preferred primer, and are stable in solution for as long as 1 day.
- (10) While the vacuum degassing procedure does not improve bond strength, it offers a number of advantages. It ensures that the adhesive is a liquid at the time of mixing, as the 7343 adhesive crystallizes on standing in the container. It ensures that the adhesive is warm at the time of mixing which prevents the curing agent from crystallizing during mixing. It prevents air oxidation of the curing agent during melting and reaction of the adhesive with atmospheric moisture. It also reduces the viscosity of the adhesive during mixing and application which allows for better mixing and easier application.
- (11) Adhesive component mixing temperatures between 160°F and 180°F have proven to be most satisfactory. Temperatures below this increase the possibility of crystallizing out the curing agent during mixing, temperatures above this range greatly reduce the pot life of the adhesive.
- (12) The use of fibrous materials or scrim cloths should be avoided because of the danger of wicking in liquid oxygen.
- (13) If a vacuum bag is used for pressure, do not use vacuum in excess of 15 in. Hg.
- (14) Bonded assemblies may be forwarded to next manufacturing operation after adhesive has gelled. However, the assembly shall not be subjected to cryogenic temperatures until it has received the full postcure.
- (15) The strength values of 2840 psi and 2165 psi are calculated on a 99% confidence limit. Mean strength 3380 psi; standard deviation of 208 samples is 524.5.

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APPENDIX C

QUALITY CONTROL DATA

APPENDIX C

QUALITY CONTROL DATA

Quality control tests were conducted on each 2-lb container of Narmco 7343 prepolymer by a test for percentage NCO and viscosity when the container was opened for use. The prepolymer described in Table 61 was found to be very uniform from one container to another, and was therefore accepted for fabrication of the bonded specimens discussed in this report.

New acceptability limits were placed on the 7343 prepolymer based on a 98% statistical probability of the first year's analysis. These new limits are 4.08% to 4.30% NCO and 20,000-cps to 30,000-cps viscosity.

Quality control tests were conducted on the prepolymers used in various studies throughout the program. Table 62 shows the results from analysis for percentage NCO when the containers were opened for use.

Table 63 compares results from an analysis of a new batch (X) of Narmco 7139 curing agent with the analysis of a previous batch (789) of curing agent.

Table 64 shows results from analysis of Narmco 7148 curing agent.

TABLE 61

QUALITY CONTROL DATA FOR NARMCO 7343 PREPOLYMER

Batch No.	Container No.	Date Analyzed	% NCO	Brookfield Viscosity @ 25°C, cps
455 ↓	107	6-06-66	4.08	28,500
	108	6-06-66	4.08	25,400
	109	6-06-66	4.08	26,600
	110	6-07-66	4.08	26,100
	111	6-15-66	4.09	25,000
	112	6-15-66	4.08	27,000
	113	6-21-66	4.14	26,900
	114	6-21-66	4.14	23,000
	115	6-21-66	4.17	27,000
	116	6-28-66	4.09	29,000
	117	6-28-66	4.11	24,360
	118	7-05-66	4.15	29,000
	119	7-05-66	4.17	29,000
	120	7-14-66	4.12	28,500
	121	7-19-66	4.12	28,000
	122	7-23-66	4.12	22,000
	123	7-23-66	4.09	22,000
	124	8-02-66	4.16	29,000
	125	8-02-66	4.17	27,500
	126	8-15-66	4.17	22,400
	127	8-15-66	4.08	22,000
592 ↓	128	8-22-66	4.12	25,500
	129	8-22-66	4.18	25,900
	130	8-22-66	4.20	24,600

TABLE 61 (Continued)

Batch No.	Container No.	Date Analysed	% NCO	Brookfield Viscosity @ 25°C CPS
592 ↓	131	9-06-66	4.26	20,600
	132	9-12-66	4.30	23,000
	133	9-12-66	4.28	24,000
	134	9-12-66	4.16	27,200
	135	9-12-66	4.30	24,000
	136	9-20-66	4.24	24,000
	137	9-20-66	4.25	26,000
	138	9-20-66	4.22	23,000
	139	9-27-66	4.25	22,000
	140	9-28-66	4.09	24,000
	141	10-04-66	4.23	23,000
	142	10-04-66	4.24	26,400
	143	10-04-66	4.23	25,200
	144	10-12-66	4.25	26,000
	145	10-17-66	4.22	29,000
	146	10-18-66	4.20	30,000
	147	10-19-66	4.16	22,400
615 ↓	148	10-24-66	4.17	22,000
	149	10-26-66	4.15	24,000
	150	10-27-66	4.20	30,400*
	151	10-31-66	4.17	29,400
	152	11-02-66	4.10	27,500
	153	11-03-66	4.13	26,500
	154	11-14-66	4.20	23,000
	158	11-16-66	4.19	24,400

* While out of standard limits considered satisfactory for production use.

TABLE 61 (Continued)

Batch No.	Container No.	Date Analyzed	% NCO	Brookfield Viscosity @ 25°C cps
615 ↓	159	12-05-66	4.19	20,000
	160	12-06-66	4.16	22,000
	161	12-08-66	4.20	21,200
	162	12-09-66	4.17	23,000
	163	12-12-66	4.20	21,300
	164	12-13-66	4.23	26,000
	165	12-13-66	4.18	27,500
	166	12-13-66	4.19	28,000
	167	12-13-66	4.19	26,200
	168	12-19-66	4.19	27,000
	169	12-19-66	4.16	26,500
	170	12-19-66	4.20	26,800
	171	12-27-66	4.16	24,800
615 ↓	172	12-27-66	4.22	20,800
689 ↓	173	12-27-66	4.18	27,600
	175	1-04-67	4.16	22,700
	176	1-05-67	4.20	27,500
	177	1-06-67	4.19	22,800
	178	1-10-67	4.15	26,000
	179	1-10-67	4.11	28,000
	180	1-10-67	4.09	27,800
↓	181	1-10-67	4.08	27,000

TABLE 62

QUALITY CONTROL DATA FOR NARMCO PREPOLYMERS

Prepolymer	Batch No.	Container No.	Date Analyzed	% NCO
Narmco 7348	165	156	11-16-66	9.42
	165	156	11-28-66	9.53
	165	174	12-27-66	9.41
Narmco X-333	183	--	1-12-67	6.09
Narmco X-334	1	--	12-01-66	9.14
Narmco X-335	44-182	--	1-11-67	2.98

TABLE 63

QUALITY CONTROL DATA FOR NARMCO 7139 CURING AGENT

Batch No.	Container No.	Date Analyzed	% Amine Purity*	% Moisture	mp, °C	Adhesive Batches
789	4	2-24-66	98.8	0.53	103-108	--
789	4	6-23-66	98.9	0.88	105.5-110	182-189
X	5	6-23-66	98.1	0.26	103.5-108	190-269
927	6	9-27-66	98.4	0.44	106.0-110	270-360

* HClO_4 method.

TABLE 64

QUALITY CONTROL DATA FOR NARMCO 7148 CURING AGENT

Batch No.	Container No.	Date Analyzed	Purity (equiv. wt.)	% of Loss on Drying	mp, °C
119	1	12-29-66	171 gm [*] /oz	1.8%**	105°-113°C

* Theoretical equivalent wt. = 150 gm/eq. Determination of actual weight is hindered by slow reactivity of this amine.

** Dried 20 hours at 90°C under vacuo.

APPENDIX D

DETERMINATION OF
SHEAR STRENGTH OF ADHESIVE-BONDED METAL-TO-METAL SPECIMENS
AT ROOM TEMPERATURE AND ELEVATED TEMPERATURES

Narmco Research & Development Division
Engineering Test Method No. 401

DETERMINATION OF
SHEAR STRENGTH OF ADHESIVE-BONDED METAL-TO-METAL SPECIMENS
AT ROOM TEMPERATURE AND ELEVATED TEMPERATURES

1. Scope

This procedure covers the determination of the tensile shear strength of adhesive-bonded metal-to-metal specimens when tested at room and at elevated temperatures.

2. Related Documents

MIL-A-5090D
Federal Test Method Standard No. 175, Method 1033
ASTM D1002

3. Test Specimens

3.1 The test specimens shall conform to the shape and dimensions shown in Figure 46.

4. Specimen Preparation

4.1 Test specimens shall be made to the final configuration (Figure 46) by cutting a bonded panel (using a band saw) (Figure 47) through the slots provided.

4.2 The cutting of the specimen shall avoid overheating and/or mechanical damage to the joints.

4.3 The specimens shall be prepared so that adherends are flat and parallel, providing a glueline of uniform thickness. Specimens with a variation in glueline thickness in excess of 20% of the average thickness shall be rejected, identified as unsuitable for testing, and returned to the requester. Specimens shall be properly aligned so that an imaginary line between the centers of the end holes bisects the overlap area. Specimens not properly aligned shall be rejected, so identified, and returned to the requester.

4.4 If the strength of the adhesive is such that it will cause deformation or failure of the metal at the pin hole, doublers may be added. For steel specimens, steel washers (0.062 in. thick with a 0.375-in. hole) spotwelded to the specimen are satisfactory. Unplated washers shall be used.

For aluminum panels, the doublers must be bonded to the specimens, preferably when the lap joint is prepared. The doublers shall be of the same material from which the specimen is made.

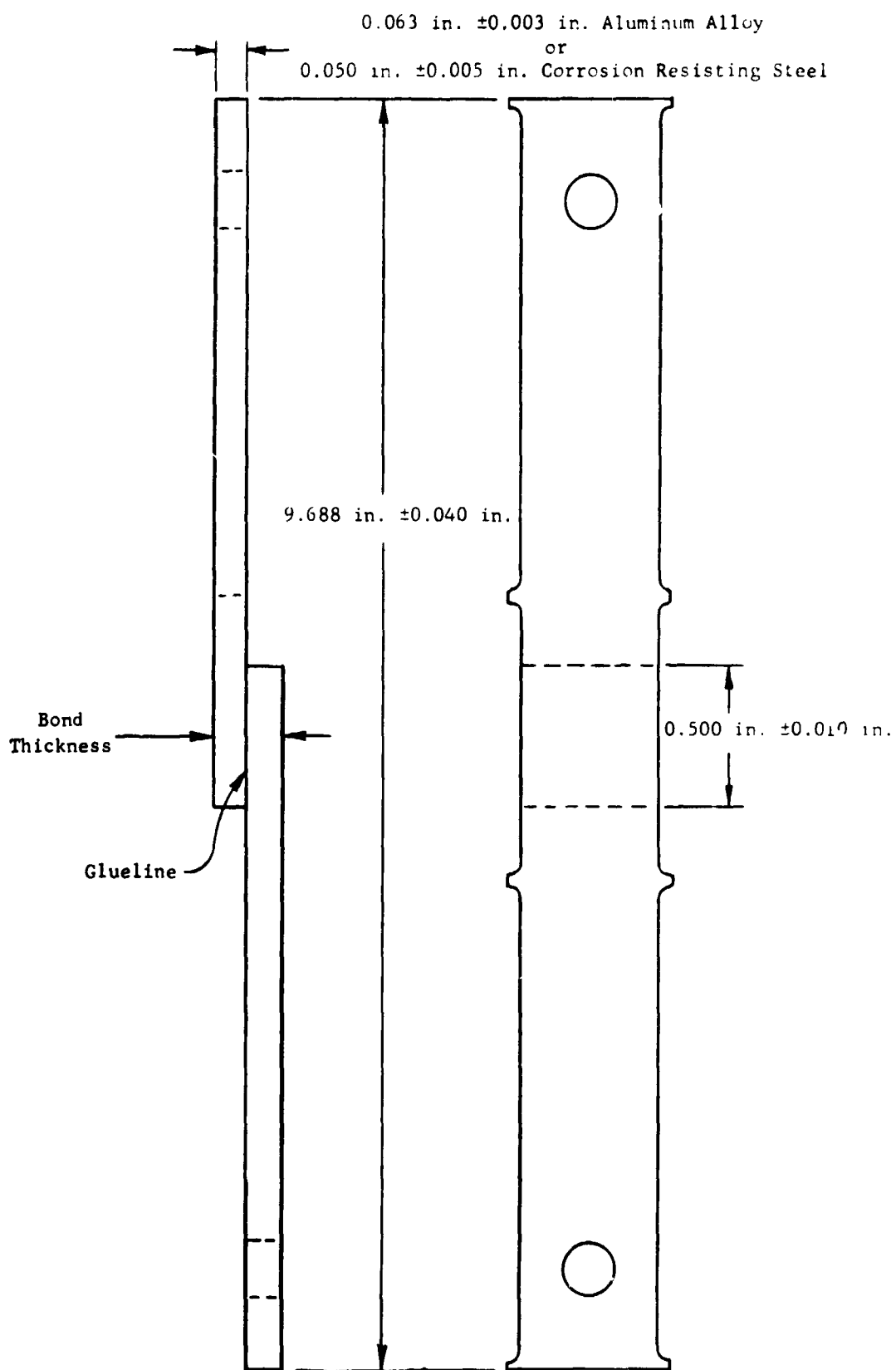


Figure 46. Test Specimen

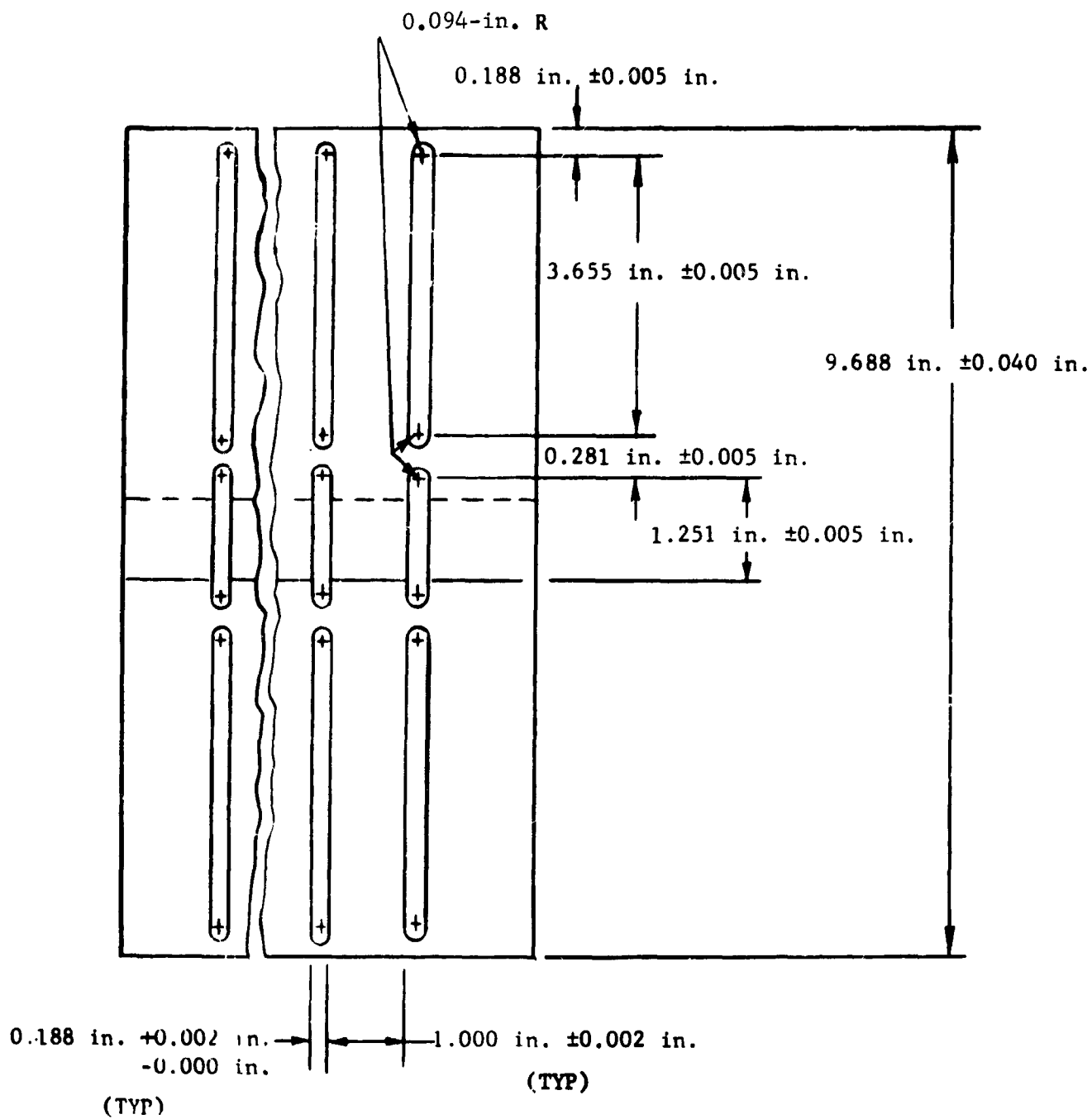


Figure 47. Preferred Assembled Panel

- 4.5 If the adhesive strength is such that failures consistently occur in the metal, a reduced bonded area may be used. When a definite strength value for the adhesive must be determined, a lap length of 0.375 in. ± 0.010 in. shall be used in place of the standard 0.500 in. ± 0.010 lap length shown in Figure 46.

5. Specimen Conditioning

- 5.1 Since conditioning is not required for metal-to-metal bonds, specimens shall be tested as soon after preparation as possible.

6. Apparatus

- 6.1 Testing Machine - A testing machine having a controllable, crosshead speed and properly calibrated load indicator shall be used.
- 6.2 Fixtures - A set of clevis type grips with pins 0.375 in. in diameter shall be used (Figure 48).
- 6.3 Thermocouple and Potentiometer - For tests at elevated temperatures, the temperature of the test specimen shall be determined utilizing a prototype, or dummy specimen. This specimen shall be prepared by placing the junction of an iron-constantan thermocouple in the center of the overlap area between the adherends prior to bonding (see Figure 49) The adherend material shall be the same as that of the specimens being tested.

The thermocouple shall be connected to a properly calibrated potentiometer.

- 6.4 Heat Source - One of the following two heat sources shall be selected for elevated temperature testing.

- 6.4.1 An oven adequate for use with the test machine and equipped with controls for maintaining the test temperature within 2% shall be used.
- 6.4.2 Quartz lamps may be used, arranged in two banks on either side of the test specimen, as shown in Figure 50. The voltage to the lamps shall be controllable with a powerstat.

7. Procedure

- 7.1 Room temperature testing - Using pertinent information from the Test Request and test specifications, prepare a test data sheet.

- 7.1.1 Measure the thickness of both adherends adjacent to the lap joint and the bond thickness (Figure 46) to the nearest 0.0001 in. and record the values.

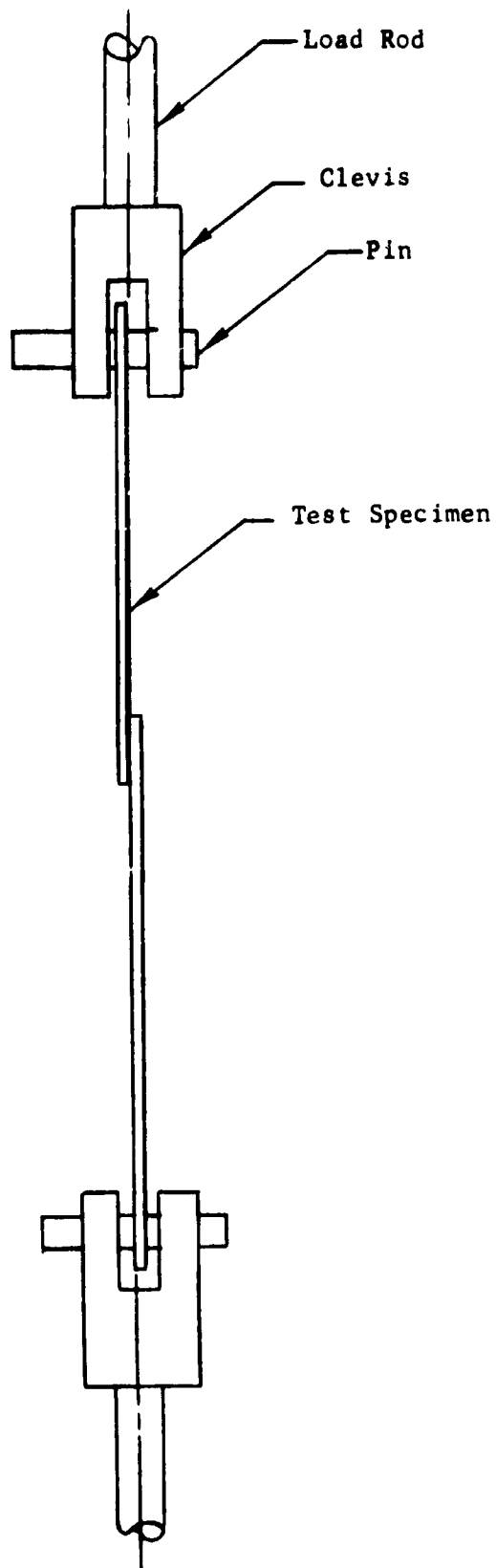


Figure 48. Test Fixture

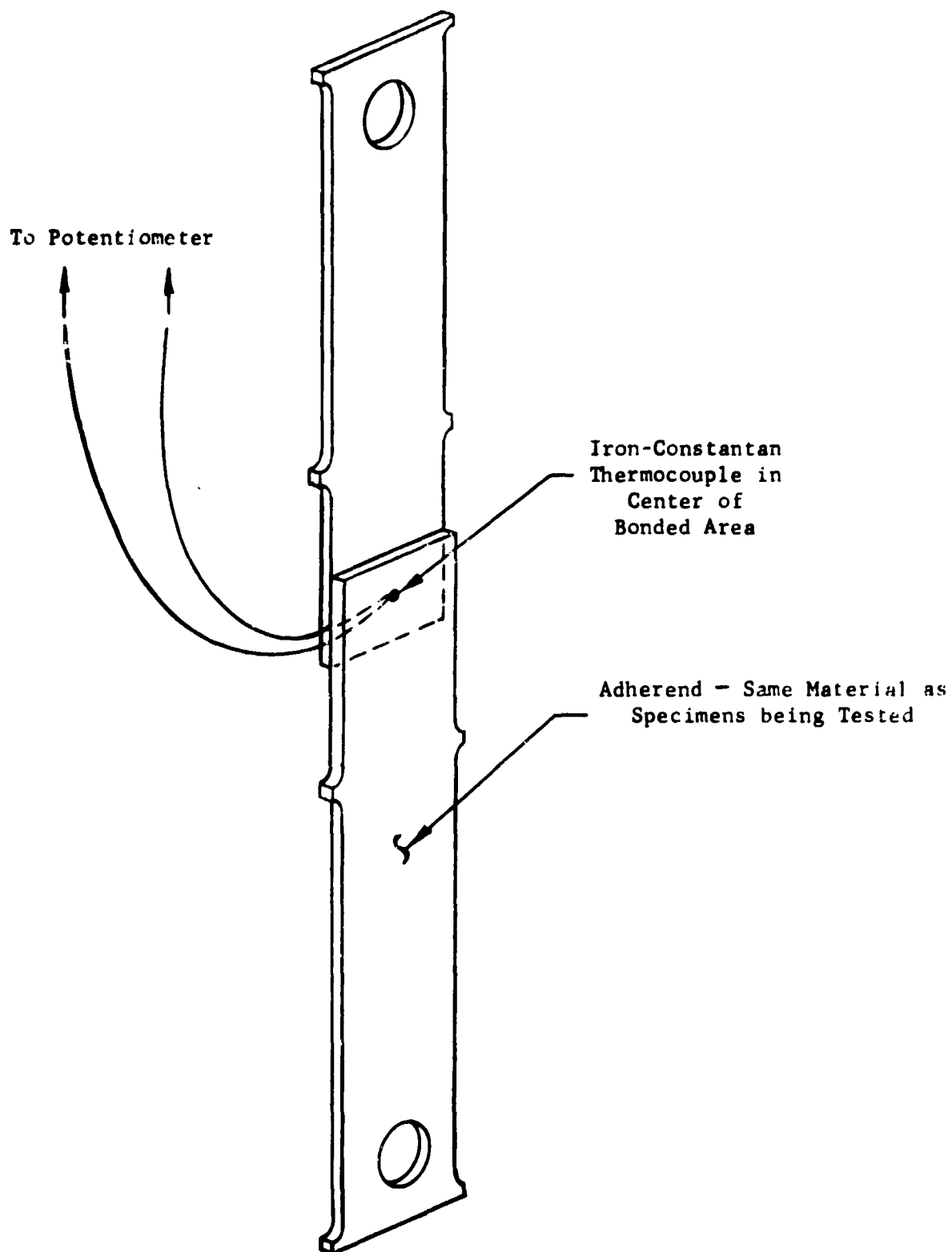


Figure 49. Prototype, or Dummy Specimen

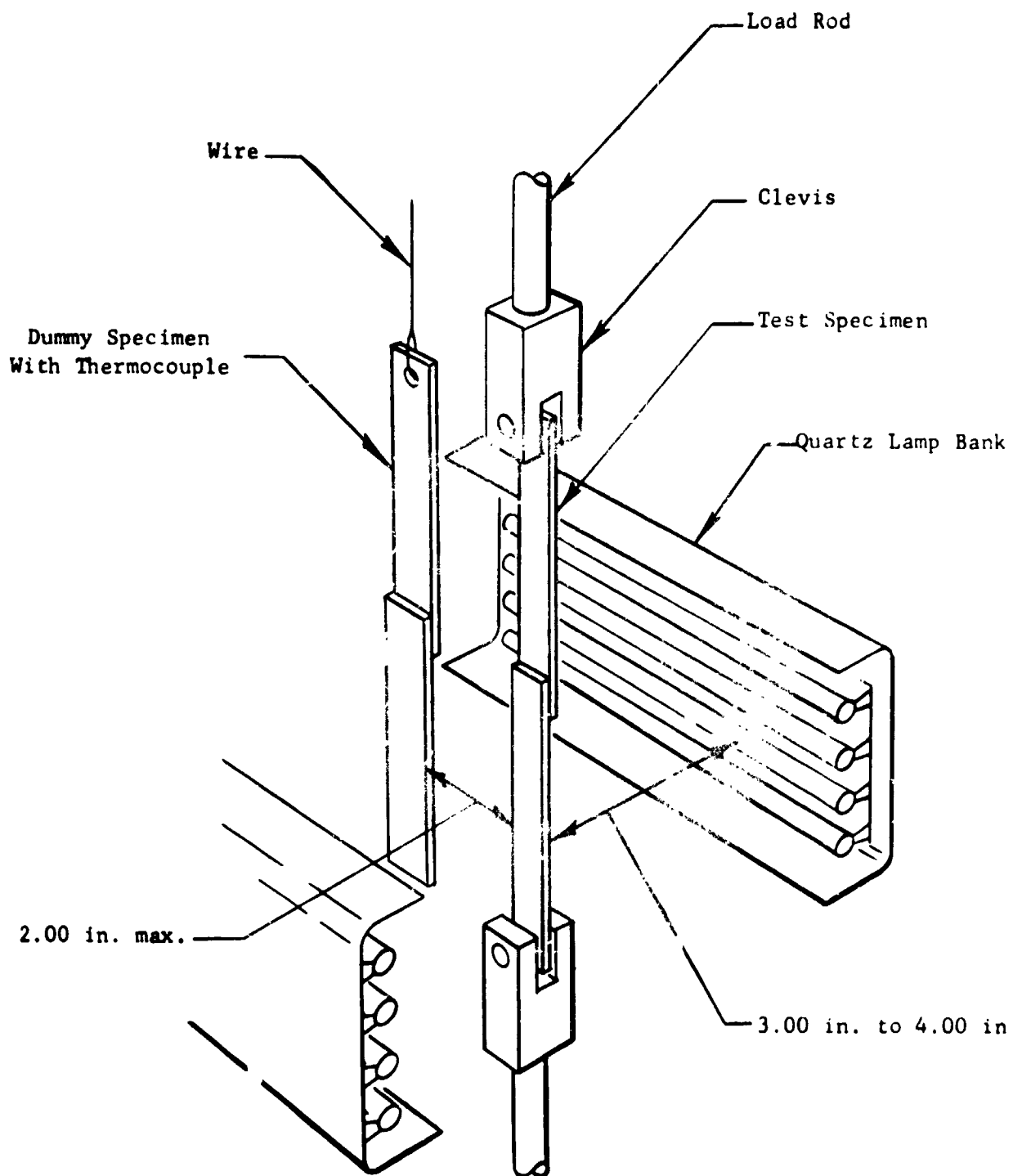


Figure 50. Test Apparatus Assembly

- 7.1.2 Determine the glueline thickness by subtracting the sum of the adherend thicknesses from the bond thickness. Record the value on the data sheet.
- Care shall be taken to avoid errors in thickness measurements due to adhesive flash, or other excess material adhering to the metal surface.
- 7.1.3 Assemble the test specimen in the grips of the testing machine so that the long axis of the test specimen coincides with the direction of applied pull through the centerline of the grip assembly (Figure 48).
- 7.1.4 Select before testing, the load range which is likely to provide the most accurate results.
- 7.1.5 Set the test machine to a crosshead speed of 0.020 in. \pm 0.002 in./minute.
- 7.1.6 Record the maximum load carried by the specimen during the test. Notation of improper failure or other pertinent comments shall be recorded.
- 7.2 Elevated Temperature Testing — Prepare a test data sheet, using pertinent information from the Test Request and test specification.
- 7.2.1 Measure the thickness of both adherends adjacent to the lap joint and the bond thickness (Figure 46) to the nearest 0.0001 in. and record the values.
- 7.2.2 Determine the glueline thickness by subtracting the sum of the adherend thicknesses from the bond thickness. Record the value on the data sheet.
- Care shall be taken to avoid errors in thickness measurements due to adhesive flash, or other excess material adhering to the metal surface.
- 7.2.3 Assemble the test specimen in the grips of the testing machine so that the long axis of the test specimen coincides with the direction of applied pull through the centerline of the grip assembly (Figure 48).
- The dummy specimen with thermocouple installed shall be suspended from a wire so that the bonded area is at the same height as the test specimen, and located not more than 2 in. from the test specimen (see Figure 50).
- 7.2.4 Select before testing, the load range which is likely to provide the most accurate results.

- 7.2.5 Set the test machine to a crosshead speed of 0.020 in. to 0.002 in./minute.
- 7.2.6 Heat the prototype specimen to the test temperature, $\pm 2\%$ as indicated by the thermocouple and potentiometer. The specimen shall be held at the test temperature for 1 minute prior to testing.
- 7.2.7 Record the maximum load carried by the specimen during the test. Notation of improper failure or other pertinent comments shall be recorded.

8. Calculations

- 8.1 Tensile Shear Strength — The tensile shear strength shall be calculated by dividing the maximum load in pounds by the shear area in square inches. The results shall be expressed in pounds per square inch (psi) and recorded to three significant figures. The following equation shall be used:

$$F_s = \frac{P}{A}$$

F_s = tensile shear strength (psi)

P = maximum load carried by the specimen (lb)

A = shear area (in.)

9. Report

- 9.1 The report shall include the following:

- 9.1.1 Complete identification of the material tested, including type, source, etc.
- 9.1.2 Complete identification of the specimen including bond length, width and area, glueline thickness, and adherend material and thickness.
- 9.1.3 Method of testing the specimen
- 9.1.4 Temperature of test
- 9.1.5 Identification of test machine and potentiometer used
- 9.1.6 Number of specimens tested
- 9.1.7 Ultimate tensile shear strength, average value

9.1.8 Nature of failure, including the average estimated percentages of failure in the cohesion of the adhesive, contact failure, and adhesion to adherend

9.1.9 Date of test

NOTES:

- (1) The test data shall be reviewed and approved by the test engineer in charge of the program before releasing it; however, "preliminary" information may be furnished to the requester with the approval of the test engineer.
- (2) The test data shall not be considered final until issued in an approved test report form.
- (3) The original test data sheet with the corresponding charts attached shall be kept on file in Engineering Test.

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APPENDIX E

DETERMINATION OF BELL PEEL STRENGTH OF ADHESIVE BONDED METAL-TO-METAL
SPECIMENS AT ROOM TEMPERATURE, CRYOGENIC AND ELEVATED TEMPERATURES

DETERMINATION OF BELL PEEL STRENGTH OF ADHESIVE BONDED METAL-TO-METAL
SPECIMENS AT ROOM TEMPERATURE, CRYOGENIC AND ELEVATED TEMPERATURES

1. Scope

This procedure covers the determination of Bell peel strength of bonded metal-to-metal specimens at room temperature, cryogenic temperatures, and elevated temperatures.

2. Related Documents

NASA brief 65-10173
ASTM D-1877-61 T
Federal Test Method No. 175, Method 1041.1

3. Test Specimens

3.1 The test specimens shall conform to the shape and dimensions shown in Figure 51.

4. Specimen Preparation

4.1 Test panels shall be made of an aluminum skin of 0.020-in. thickness bonded to an aluminum base of 0.063-in. thickness as shown in Figure 51. Three specimens shall be cut from the panel.

4.2 Test specimens shall be made to the final configuration (see Figure 51) by cutting the bonded panel (using a band saw) to the required dimensions and drilling a 0.375-in. hole as shown.

4.3 Overheating or mechanical damage to the bonded joint should be avoided during cutting and drilling.

5. Apparatus

5.1 Testing Machine — A testing machine having a controllable cross-head speed and properly calibrated load indicator and recorder shall be used.

5.2 Fixture — The test fixture is shown in Figure 52 with the specimen in place prior to testing.

6. Test Procedure

6.1 Room Temperature Testing

6.1.1 A test data sheet shall be prepared using pertinent information from the Engineering Test Request and test specifications.

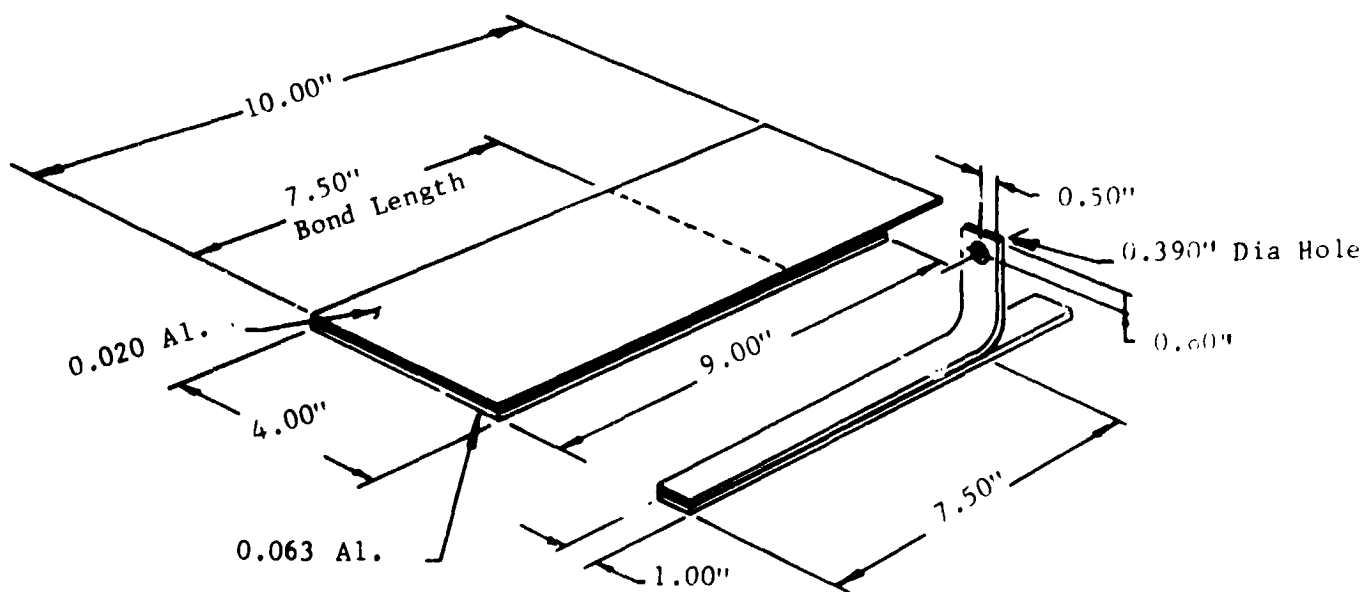


Figure 51. Test Panel and Finished Test Specimen

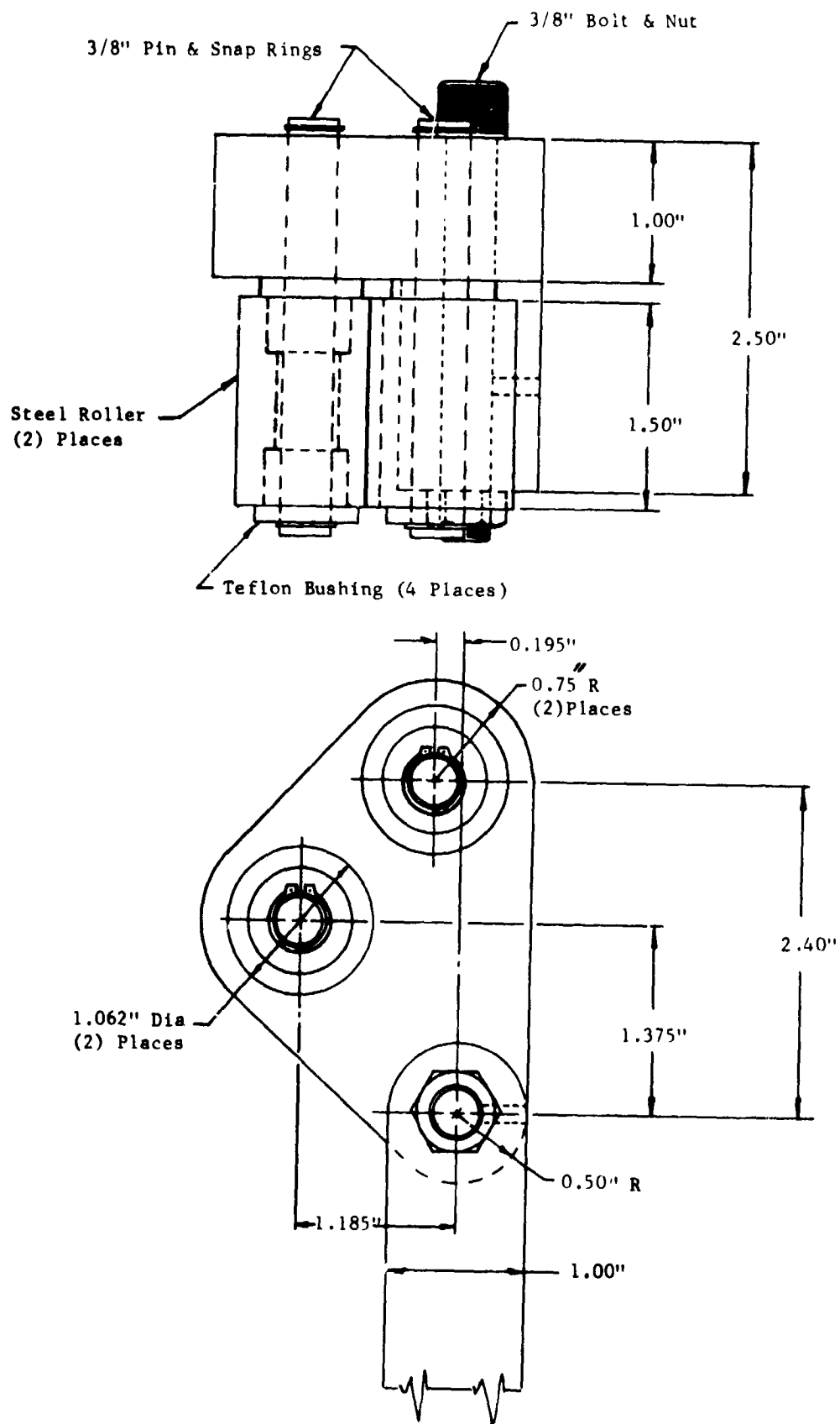


Figure 52. Peel Test Fixture

- 6.1.2 The specimen thickness shall be measured and recorded to the nearest 0.0005 in.
- 6.1.3 The specimen width shall be measured and recorded to the nearest 0.010 in.
- 6.1.4 The test machine speed shall be set to produce a specimen bond separation of 5.0 in./minute and the recorder set at 5.0 in./minute chart travel.
- 6.1.5 The test specimen shall be inserted into the test fixture as shown in Figures 52 and 53.
- 6.1.6 The recorder shall be adjusted to zero and the test machine started. The specimen shall be peeled for a minimum length of 7 in.

6.2 Cryogenic Testing

- 6.2.1 A test data sheet shall be prepared using pertinent information from the Engineering Test Request and test specifications.
- 6.2.2 The specimen thickness shall be measured and recorded to the nearest 0.0005 in.
- 6.2.3 The specimen width shall be measured and recorded to the nearest 0.010 in.
- 6.2.4 The test machine speed shall be set to produce a specimen bond separation of 5.0 in./minute and the recorder set at 5.0 in./minute of chart travel.
- 6.2.5 The test specimen shall be inserted into the test fixture as shown in Figures 52 and 53.
- 6.2.6 The test fixture and specimen shall be immersed in the cryogenic liquid for a period of time sufficient to insure temperature stabilization of the specimen.
- 6.2.7 The recorder shall be adjusted to zero and the test machine started. The specimen shall be peeled for a minimum length of 7 in.

6.3 Elevated Temperature Testing

- 6.3.1 A test data sheet shall be prepared using pertinent information from the Engineering Test Request and test specifications.
- 6.3.2 The specimen thickness shall be measured and recorded to the nearest 0.0005 in.

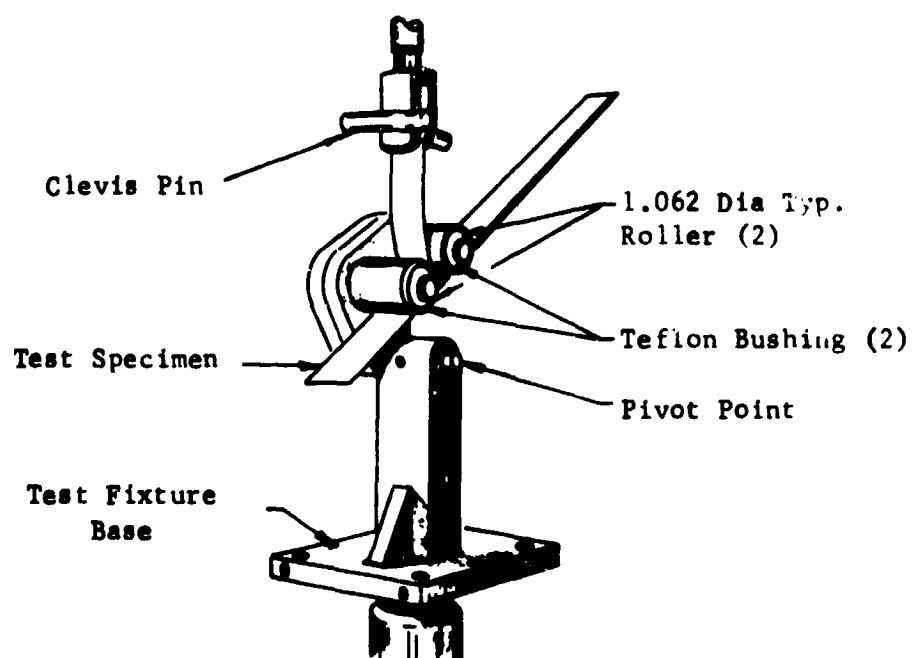


Figure 53. Test Fixture with Specimen Installed for Room Temperature Test. (Fixture is installed in special container and submerged in liquid nitrogen for -320°F testing)

- 6.3.3 The specimen width shall be measured and recorded to the nearest 0.010 in.
- 6.3.4 The test machine speed shall be set to produce a specimen bond separation of 5.0 in./minute and the recorder set at 5.0 in./minute of chart travel.
- 6.3.5 The test specimen shall be inserted into the test fixture as shown in Figures 52 and 53.
- 6.3.6 The test fixture and specimen shall be enclosed in a suitable oven and a thermocouple attached to the test specimen by means of a small alligator clip. The test temperature as indicated by the thermocouple and potentiometer shall be maintained to $\pm 2\%$. This temperature shall be maintained for 1 minute prior to testing.
- 6.3.7 The recorder shall be adjusted to zero and the test machine started. The specimen shall be peeled for a minimum length of 7 in.

7. Calculation

The average peeling load in pounds per inch of specimen width required to separate the adherends shall be determined from the recording for the first 7 in. of peel after the initial peak.

NOTE: The average load shall be calculated by recording the load at 1-in. intervals of crosshead motion after the initial peak. a minimum of seven points shall be used to determine the average.

8. Report

8.1 The report shall include the following:

- 8.1.1 Complete identification of the material tested, including type, source, etc.
- 8.1.2 Complete identification of the specimen including adhesive thickness and adherend material
- 8.1.3 Method of testing the specimen
- 8.1.4 Temperature of test
- 8.1.5 Identification of test machine and potentiometer used
- 8.1.6 Number of specimens tested
- 8.1.7 Peel strength in pounds per inch of specimen width

8.1.8 Nature of the failure including percent adhesive failure

8.1.9 Date and time of test

NOTES:

- (1) The test data shall be reviewed and approved by the test engineer in charge of the program before releasing it; however, "preliminary" information may be furnished to the requester with the approval of the test engineer.
- (2) The test data shall not be considered final until issued in an approved test report form.
- (3) The original test data sheet with the corresponding charts attached shall be kept on file in Engineering Test.

APPENDIX F
SOURCE OF MATERIALS LIST

<u>Product</u>	<u>Type</u>	<u>Composition</u>	<u>Source of Supply</u>
Narmco 7343	Polyurethane	100% Solids	WHITTAKER CORPORATION Narmco Materials Division Costa Mesa, California
Narmco 7348	" "	" "	" "
Narmco X333	" "	" "	WHITTAKER CORPORATION Narmco Research & Development Division San Diego, California
Narmco X334	" "	" "	" "
Narmco X335	" "	" "	" "
Narmco 7139	Aromatic Amine	" "	WHITTAKER CORPORATION Narmco Materials Division Costa Mesa, California
Narmco 7148	" "	" "	" "